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Michel Addition Curing Chemistries for Sulfur-Containing Polymer Compositions

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None

References Cited
U.S. Patent Documents
4,659,570 A 11/1977 Oswald

Other Reissue Documents

FOREIGN PATENT DOCUMENTS

OTHER PUBLICATIONS


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ABSTRACT

The use of Michael addition curing chemistries in compositions comprising sulfur-containing polymers such as polythioethers and polysulfides useful in aerospace sealant applications are disclosed. Sulfur-containing adducts comprising terminal Michael acceptor groups are also disclosed.

21 Claims, No Drawings
MICHAEL ADDITION CURING CHEMISTRIES FOR SULFUR-CONTAINING POLYMER COMPOSITIONS

CROSS-REFERENCE TO RELATED APPLICATION

This application is a continuation application of U.S. patent application Ser. No. 13/529,237 filed on Jun. 21, 2012, now allowed, which is incorporated by reference in its entirety.

FIELD

The present disclosure relates to the use of Michael addition curing chemistries in compositions comprising sulfur-containing polymers, such as polythioethers and polysulfides, useful in aerospace sealant applications. The disclosure also relates to sulfur-containing adducts having terminal Michael acceptor groups and compositions thereof.

BACKGROUND

Sealants useful in aerospace and other applications must satisfy demanding mechanical, chemical, and environmental requirements. The sealants can be applied to a variety of surfaces including metal surfaces, primer coatings, intermediate coatings, finishing coatings, and aged coatings. In sealants such as those described in U.S. Pat. No. 6,123,179 an amine catalyst is used to provide a cured product. Such systems typically cure in over two hours and although exhibiting acceptable fuel resistance and thermal resistance for many applications, a faster curing rate and improved performance is desirable.

SUMMARY

Michael addition curing chemistries are often used in acrylic-based polymer systems and as disclosed in U.S. Pat. No. 3,138,753 have been adapted for use in polythioether compositions. Application of Michael addition curing chemistries to sulfur-containing polymers not only results in cured sealants with faster cure rates and enhanced performance including fuel resistance and thermal resistance, but also provides a sealant with improved physical properties, such as elongation.

In a first aspect, polythioether adducts comprising at least two terminal Michael acceptor groups are provided.

In a second aspect, compositions are provided comprising a polythioether polymer comprising at least two terminal groups reactive with Michael acceptor groups; and a compound having at least two Michael acceptor groups.

In a third aspect, compositions are provided comprising a polythioether adduct provided by the present disclosure and a curing agent comprising at least two terminal groups that are reactive with Michael acceptor groups.

In a fourth aspect, compositions are provided comprising (a) the sulfur-containing adduct provided by the present disclosure; (b) a sulfur-containing polymer comprising at least two terminal groups reactive with Michael acceptor groups; and (c) a monomeric compound having at least two Michael acceptor groups.

In a fifth aspect, hydroxyl-terminated sulfur-containing adducts are provided comprising the reaction products of reactants comprising (a) a sulfur-containing Michael acceptor adduct provided by the present disclosure; and (b) a compound having a hydroxy group and a group that is reactive with the terminal groups of the sulfur-containing Michael acceptor adduct.

In a sixth aspect, compositions are provided comprising (a) a hydroxyl-terminated sulfur-containing adduct provided by the present disclosure; and (b) a polyisocyanate curing agent.

In a seventh aspect, amine-terminated sulfur-containing adducts are provided comprising the reaction products of reactants comprising (a) a sulfur-containing Michael acceptor adduct provided by the present disclosure; and (b) a compound having a amine group and a group that is reactive with the terminal groups of the sulfur-containing Michael acceptor adduct.

In an eighth aspect, compositions are provided comprising (a) an amine-terminated sulfur-containing adduct provided by the present disclosure; and (b) a polyisocyanate curing agent.

In a ninth aspect, cured sealants comprising a composition provided by the present disclosure are provided.

In a tenth aspect, apertures sealed with a composition provided by present disclosure are provided.

In an eleventh aspect, methods of sealing an aperture are provided comprising (a) applying a composition provided by the present disclosure formulated as a sealant to at least one surface defining an aperture; (b) assembling the surfaces defining the aperture; and (c) curing the composition to provide a sealed aperture.

DETAILED DESCRIPTION

Definitions

For purposes of the following description, it is to be understood that embodiments provided by the present disclosure may assume various alternative variations and step sequences, except where expressly specified to the contrary. Moreover, other than in the examples, or where otherwise indicated, all numbers expressing, for example, quantities of ingredients used in the specification and claims are to be understood as being modified in all instances by the term “about.” Accordingly, unless indicated to the contrary, the numerical parameters set forth in the following specification and attached claims are approximations that may vary depending upon the desired properties to be obtained. At the very least, and not as an attempt to limit the application of the doctrine of equivalents to the scope of the claims, each numerical parameter should at least be construed in light of the number of reported significant digits and by applying ordinary rounding techniques.

Notwithstanding that the numerical ranges and parameters setting forth the broad scope of the invention are approximations, the numerical values set forth in the specific examples are reported as precisely as possible. Any numerical value, however, inherently contains certain errors necessarily resulting from the standard variation found in their respective testing measurements.

Also, it should be understood that any numerical range recited herein is intended to include all sub-ranges encompassed therein. For example, a range of “1 to 10” is intended to include all sub-ranges between (and including) the recited minimum value of about 1 and the recited maximum value of about 10, that is, having a minimum value equal to or greater than about 1 and a maximum value of equal to or less than about 10. Also, in this application, the use of “or” means “and/or” unless specifically stated otherwise, even though “and/or” may be explicitly used in certain instances.
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A dash ("—") that is not between two letters or symbols is used to indicate a point of bonding for a substituent or between two atoms. For example, —CONH₂ is bonded to another chemical moiety through the carbon atom.

"Alkenyl" refers to a diradical of a saturated, branched or straight-chain, acyclic hydrocarbon group, having, for example, from 1 to 18 carbon atoms (C₁₋₁₈), from 1 to 14 carbon atoms (C₁₋₁₄), from 1 to 6 carbon atoms (C₁₋₆), from 1 to 4 carbon atoms (C₁₋₄), or from 1 to 3 hydrocarbon atoms (C₁₋₃). It will be appreciated that a branched alkyl has a minimum of three carbon atoms. In certain embodiments, the alkenyl is C₂₋₄, alkanyl, C₉₋₁₂, alkanyl, C₈₋₁₂ alkanyl, C₉₋₁₂ alkanyl, and in certain embodiments, C₉₋₁₂ alkanyl. Examples of alkenyl groups include methane-diyl (—CH₂—), ethane-1,2-diyl (—CH₂—CH₂—), propane-1,3-diyl and iso-propane-1,2-diyl (e.g., —CH₃CH₂—CH₃ and —CH₂CH₂CH₃), butane-1,4-diyl (—CH₂CH₂CH₂—CH₂—), pentane-1,5-diyl (—CH₂CH₂CH₂CH₂—CH₂—), hexane-1,6-diyl (—CH₂CH₂CH₂CH₂CH₂—CH₂—), heptane-1,7-diyl, octane-1,8-diyl, nonane-1,9-diyl, decane-1,10-diyl, dodecane-1,1₂-diyl, and the like.

"Alkancyclocloalkane" refers to a saturated hydrocarbon group having one or more cycloalkyl and/or cycloalkanediyl groups and one or more alkyl and/or alkanyl groups, where cycloalkyl, cycloalkanediyl, alkyl, and alkanyl are defined herein. In certain embodiments, each cycloalkyl and/or cycloalkanediyl group(s) C₆₋₈, C₈₋₁₀, and in certain embodiments, cyclohexyl or cyclohexanediyl. In certain embodiments, each alkyl and/or alkanyl group(s) C₁₋₆, C₁₋₄, C₁₋₃, and in certain embodiments, methyl, methanediyl, ethyl, or ethane-1,2-diyl. In certain embodiments, the alkancyclocloalkane group is C₆₋₈ alkancyclocloalkane, C₈₋₁₀ alkancyclocloalkane, C₁₋₄ alkancyclocloalkane, C₁₋₃ alkancyclocloalkane, C₁₋₂ alkancyclocloalkane, C₁₋₁ alkancyclocloalkane, and in certain embodiments, benzene-diyl.

"Cyloalkyl" refers to a saturated monocyclic or poly cyclic hydrocarbon group. In certain embodiments, the cycloalkyl group is C₅₋₁₂ cycloalkyl, C₇₋₁₂ cycloalkyl, C₉₋₁₂ cycloalkyl, and in certain embodiments, C₉₋₁₂ cycloalkyl. Examples of cycloalkanediyl groups include cyclohexane-1,4-diyl, cyclohexane-1,3-diyl, and cyclohexane-1,2-diyl.

"Heteroatom" refers to an atom other than hydrogen, such as nitrogen, oxygen, sulfur, phosphorus, or selenium. In certain embodiments, the heteroatom is selected from N, O, S, or P.
vinyl sulfone, a quinone, an enamine, a ketimine, oxazolidine, and an acrylate. Other examples of Michael acceptors are disclosed in Mather et al., Prog. Polym. Sci. 2006, 31, 487-531, and include acrylate esters, acrylonitrile, acrylamides, maleimides, alkyl methacrylates, cyanacrylates. Other Michael acceptors include vinyl ketones, α,β-unsaturated aldehydes, vinyl phosphonates, acrylonitrile, vinyl pyridines, certain azo compounds, β-keto acylenes and acetylene esters. In certain embodiments, a Michael acceptor group is derived from a vinyl ketone and has the structure of Formula (2):

\[ \text{SO}(-C(R))=CH_2 \]  

where each R is independently selected from hydrogen, fluorine, and C1-3 alkyl. In certain embodiments, each R is hydrogen. In certain embodiments, a Michael acceptor or Michael acceptor group does not encompass acrylates. A “Michael acceptor compound” refers to a compound comprising at least one Michael acceptor. In certain embodiments, a Michael acceptor compound is divinyl sulfone, and a Michael acceptor compound is vinylsulfanyl (—SO2CH=CH2). As used herein, “polymer” refers to oligomers, homopolymers, and copolymers. Unless stated otherwise, molecular weights are number average molecular weights for polymeric materials indicated as “Mn” as determined, for example, by gel permeation chromatography using a polystyrene standard in an art-recognized manner.

“Substituted” refers to a group in which one or more hydrogen atoms are each independently replaced with the same or different substituents(s). In certain embodiments, the substituent is selected from halogen, —SO(CH3)OH, —SO(OH), —S(OH), —S(O2)H, —S(O)2H, wherein R is C1-3 alkyl, —COOH, —NO2, —NR, wherein each R is independently selected from hydrogen and C1-3 alkyl, —CN, —O, C1-6 alkyl, —CF3, —OH, phenyl, C2-6 heteroaryl, C2-6 heteroaromatic, C2-6 alkoxy, —CONH2, —CONH—, —CON(=O)R, and —COR wherein R is C1-6 alkyl. In certain embodiments, the substituent is chosen from —OH, —NH2, and C1-3, alkyl.

Reference is now made to certain embodiments of sulfur-containing adducts having terminal Michael acceptor groups, polymers, compositions, and methods. The disclosed embodiments are not intended to be limiting of the claims. To the contrary, the claims are intended to cover all alternatives, modifications, and equivalents. **Sulfur-Containing Adducts**

Sulfur-containing adducts provided by the present disclosure comprise terminal Michael acceptor groups. Sulfur-containing polymers useful herein include, for example, polythioethers, polysulfides, and combinations thereof. Examples of suitable polythioethers are disclosed in U.S. Pat. No. 6.123.179. Examples of suitable polysulfides are disclosed in U.S. Pat. No. 4.623.711. In certain embodiments, a sulfur-containing group may be difunctional, and in certain embodiments, may have a functionality greater than 2 such as 3, 4, 5, or 6. A sulfur-containing adduct may comprise a mixture of sulfur-containing adducts having different functionalities characterized by an average functionality from 2.05 to 6, from 2.1 to 4, from 2.1 to 3, from 2.2 to 2.8, and in certain embodiments, from 2.4 to 2.6. A sulfur-containing adduct may comprise a combination of adducts having different numbers of terminal Michael acceptor groups characterized, for example, by an average Michael acceptor functionality of from 2.05 to 6, from 2.1 to 4, from 2.1 to 3, from 2.2 to 2.8, and in certain embodiments, from 2.4 to 2.6. In certain embodiments, a sulfur-containing adduct comprises a polythioether adduct characterized by a polythioether having at least two terminal Michael acceptor groups. In certain embodiments, a sulfur-containing adduct comprises a polythioether adduct comprising:

(a) a backbone comprising the structure of Formula (1):

\[ R_1=\text{CH}_3 \]

(1)

where (i) each R1 is independently selected from a C5-10 n-alkanediyl group, a C6-8 branched alkanediyl group, a C6-8 cycloalkanediyl group, a C9-10 alkanecycloalkanediyl group, a heterocyclic group, a \( (-\text{CHR}^2) \cdots \text{X} \cdots \text{CHR}^1 \) group, wherein each R1 is independently selected from hydrogen and methyl, (ii) each R2 is independently selected from a C5-10 n-alkyl group, a C6-8 branched alkanediyl group, a C6-8 cycloalkanediyl group, a C9-14 alkanecycloalkanediyl group, a heterocyclic group, and a \( (-\text{CHR})^2 \cdots \text{X} \cdots \text{CHR} \) group, (iii) each X is independently selected from O, S, and —NR2 group, in which R2 is selected from H and a methyl group; (iv) m ranges from 0 to 50; (v) n is an integer ranging from 1 to 60; (vi) p is an integer ranging from 2 to 6; (vii) q is an integer ranging from 1 to 5; and (viii) r is an integer ranging from 2 to 10; and (b) at least two terminal Michael acceptor groups.

In certain embodiments of a compound of Formula (1), R1 is \( (-\text{CHR}^2) \cdots \text{X} \cdots \text{CHR}^1 \) wherein each X is independently selected from —O— and —S—. In certain embodiments wherein R1 is \( (-\text{CHR}^2) \cdots \text{X} \cdots \text{CHR}^1 \) wherein each X is —O— and in certain embodiments, each X is —S—.

In certain embodiments of a compound of Formula (1), R1 is \( (-\text{CHR}^2) \cdots \text{X} \cdots \text{CHR}^1 \) wherein each X is independently selected from —O— and —S—. In certain embodiments wherein R1 is \( (-\text{CHR}^2) \cdots \text{X} \cdots \text{CHR}^1 \) wherein each X is —O— and in certain embodiments, each X is —S—.

In certain embodiments, R1 in Formula (3a) is \( (-\text{CHR}^2) \cdots \text{X} \cdots \text{CHR}^1 \) wherein p is 2, X is O, q is 2, r is 2, R2 is ethanediol, m is 2, and n is 9.

Michael acceptor groups are well known in the art. In certain embodiments, a Michael acceptor group comprises an activated alkene, such as an alkylidene group proximate to an electron-withdrawing group such as an enone, nitro, halo, nitrite, carbonyl, or nitro group. In certain embodiments, a Michael acceptor group is selected from a vinyl ketone, a vinyl sulfone, a quinone, an enamine, a kettimine, an alidine, and an oxazolidine. In certain embodiments, each of the Michael acceptor groups may be the same and in certain embodiments, at least some of the Michael acceptor groups are different.

In certain embodiments, a Michael acceptor group is derived from a vinyl sulfone and has the structure of Formula (2):

\[ \text{CH}_2=\text{C}(-\text{R}^2)=\text{SO}(-\text{R}^3)=\text{CH}_2 \]  

(2)

wherein each R is independently selected from hydrogen and C1-3 alkyl. In certain embodiments of Formula (2), each R is hydrogen.

In certain embodiments where the sulfur-containing adduct comprises a polythioether adduct, the polythioether adduct is selected from a polythioether adduct of Formula (3), a polythioether adduct of Formula (3a), and a combination thereof:

\[ R^2=\text{R}^1=\text{S}(-\text{CH}(_2))_\text{m}=-\text{R}^2=\text{O}(-\text{R}^3)=\text{CH}_2 \]

(3)

\[ \text{R}^2=\text{R}^1=\text{S}(-\text{CH}(_2))_\text{m}=-\text{R}^2=\text{O}(-\text{R}^3)=\text{CH}_2 \]

(3a)
In certain embodiments, a sulfur-containing adduct comprises a polysulfide adduct comprising at least two terminal Michael acceptor groups.

As used herein, the term polysulfide refers to a polymer that contains one or more disulfide linkages, i.e., $-[S-S]-$, linkages, in the polymer backbone and/or in pendant positions on the polymer chain. In certain embodiments, the polysulfide polymer will have two or more sulfur-sulfur linkages. Suitable polysulfides are commercially available, for example, from Akzo Nobel and Toray Fine Chemicals under the names Thiochlor-LP® and Thioplast®. Thioplast® products are available in a wide range of molecular weights ranging, for example, from less than 1,100 to over 8,000, with molecular weight being the average molecular weight in grams per mole. In some cases, the polysulfide has a number average molecular weight of 1,000 to 4,000. The crosslink density of these products also varies, depending on the amount of crosslinking agent used. The $-SH$ content, i.e., thiol or mercaptan content, of these products can also vary. The mercaptan content and molecular weight of the polysulfide can affect the cure speed of the polymer, with cure speed increasing with molecular weight.

In certain embodiments provided by the present disclosure, a polysulfide composition comprises: (a) from 90 mole percent to 25 mole percent of mercaptan terminated disulfide polymer of the Formula HS(RSS)S$R-SH$; and (b) from 10 mole percent to 75 mole percent of diethyl formal mercaptan terminated polysulfide polymer of the Formula HS(RSS)S$R-SH$, wherein R is $-CH_2CH_2O-CH_2O-CH_2CH_2-; R$ is a divalent member selected from an alkyl of from 2 to 12 carbon atoms, alkyl thioether of from 4 to 20 carbon atoms, alkyl ether of from 4 to 20 carbon atoms and one oxygen atom, alkyl ether of from 4 to 20 carbon atoms and from 2 to 4 oxygen atoms each of which is separated from the other by at least 2 carbon atoms, aliphatic of from 6 to 12 carbon atoms, and aromatic lower alkyl; and the value of $m$ and $n$ is such that the diethyl formal mercaptan terminated polysulfide polymer and the mercaptan terminated disulfide polymer have an average molecular weight of from 1,000 Daltons to 4,000 Daltons, such as 1,000 Daltons to 2,500 Daltons. Such polymeric mixtures are described in U.S. Pat. No. 4,623,711 at col. 4, line 18 to col. 8, line 35, the cited portion of which is incorporated by reference herein. In some cases, R in the above formula is $-CH_2CH_2O-CH_2O-CH_2CH_2-; -CH_2O-CH_2O-CH_2CH_2-; -CH_2O-CH_2O-CH_2CH_2-; -CH_2O-CH_2O-CH_2CH_2-; -CH_2O-CH_2O-CH_2CH_2-; -CH_2O-CH_2O-CH_2CH_2-; -CH_2O-CH_2O-CH_2CH_2-; -CH_2O-CH_2O-CH_2CH_2-; -CH_2O-CH_2O-CH_2CH_2-; or $-CH_2O-CH_2O-CH_2CH_2-$. In certain embodiments, a sulfur-containing adduct comprises a polythioether adduct comprising at least two terminal Michael acceptor groups, a polysulfide adduct comprising at least two terminal Michael acceptor groups, or a combination thereof.

In certain embodiments, sulfur-containing Michael acceptor adds provided by the present disclosure comprise the reaction products of reactants comprising: (a) a sulfur-containing polymer; and (b) a compound having a Michael acceptor group and a group that is reactive with a terminal group of the sulfur-containing polymer.

In certain embodiments, the sulfur-containing polymer is selected from a polythioether and a polysulfide, and a combination thereof. In certain embodiments a sulfur-containing polymer comprises a polythioether; and in certain embodiments, a sulfur-containing polymer comprises a polysulfide. A sulfur-containing polymer may comprise a mixture of different polythioethers and/or polysulfides, and the polythioethers and/or polysulfides may have the same or different functionality. In certain embodiments, a sulfur-containing polymer has an average functionality from 2 to 6, from 2 to 4,
from 2 to 3, and in certain embodiments, from 2.05 to 2.5. For example, a sulfur-containing polymer can be selected from a difunctional sulfur-containing polymer, a trifunctional sulfur-containing polymer, and a combination thereof.

In certain embodiments, a sulfur-containing polymer is terminated with a group that is reactive with the terminal reactive group of the compound (b). In certain embodiments, the compound having a Michael acceptor group has two Michael acceptor groups, and the terminal groups of the sulfur-containing polymer are reactive with Michael acceptor groups such as a thiol group. A sulfur-containing polymer may comprise terminal thiol groups, terminal alkenyl groups, or terminal epoxy groups.

In certain embodiments, a sulfur-containing polymer is thiol-terminated. Examples of thiol-functional polyhydrothiols are disclosed, for example in U.S. Pat. No. 6,172,179. In certain embodiments, a thiol-functional polythioether comprises Permapol® P3.1E, available from PRC-Desoto International Inc., Sylmar, Calif.

In certain embodiments, a sulfur-containing polymer comprises a polyhydrothio ether comprising:

(a) a backbone comprising the structure of Formula (1):

\[ \text{R}^1 \text{--S--CH}_2 \text{--O--[R}^2 \text{--O--[CH}_2 \text{]} \text{n} \text{--S--R}^1 \text{--} \]

wherein:
(i) each R\(^1\) is independently selected from a C\(_{2-10}\) n-alkanediyl group, a C\(_{3-6}\) branched alkanediyl group, a C\(_{6-8}\) cycloalcanediyl group, a C\(_{8-10}\) alkanecycloalcanediyl group, a heterocyclic group, a \([--\text{CHR}^3--\text{O}--\text{CHR}^3--\text{]} \text{n} \text{--S--R}^1\]

(ii) each R\(^2\) is independently selected from a C\(_{2-10}\) n-alkanediyl group, a C\(_{3-6}\) branched alkanediyl group, a C\(_{6-8}\) cycloalcanediyl group, a C\(_{8-10}\) alkanecycloalcanediyl group, a heterocyclic group, and a \([--\text{CHR}^3--\text{O}--\text{CHR}^3--\text{]} \text{n} \text{--S--R}^1\]

(iii) each X is independently selected from O, S, and a \(-\text{NR}^2\text{O}--\) group, in which R\(^2\) is selected from H and a methyl group;

(iv) n ranges from 0 to 50;

(v) \(q\) is an integer ranging from 1 to 60;

(vi) \(p\) is an integer ranging from 2 to 6;

(vii) \(r\) is an integer ranging from 1 to 5; and

(viii) \(s\) is an integer ranging from 2 to 10.

In certain embodiments, a sulfur-containing polymer comprises a polyhydrothio ether selected from a polyhydrothio ether of Formula (4), a polyhydrothio ether of Formula (4a), and a combination thereof:

\[ \text{HS--R}^1 \text{--S--CH}_2 \text{--O--[R}^2 \text{--O--[CH}_2 \text{]} \text{n} \text{--S--R}^1 \text{--SH} \]

\[ \text{HS--R}^1 \text{--S--CH}_2 \text{--O--[R}^2 \text{--O--[CH}_2 \text{]} \text{n} \text{--S--R}^1 \text{--S--V}^1 \text{--]} \text{B} \]

wherein:

- each R\(^1\) independently is selected from C\(_{2-10}\) alkanediyl, C\(_{3-6}\) cycloalcanediyl, C\(_{6-8}\) alkanecycloalcanediyl, C\(_{5-8}\) heterocyclic alkanediyl, and \([--\text{CHR}^3--\text{O}--\text{CHR}^3--\text{]} \text{n} \text{--S--R}^1\]

- each R\(^2\) is independently selected from hydrogen and methyl;

- each X is independently selected from O, S, and a \(-\text{NR}^2\text{O}--\) group, in which R\(^2\) is selected from hydrogen and methyl;

- each R\(^3\) is independently selected from C\(_{1-10}\) alkanediyl, C\(_{3-6}\) cycloalcanediyl, C\(_{6-8}\) alkanecycloalcanediyl, and \([--\text{CHR}^3--\text{O}--\text{CHR}^3--\text{]} \text{n} \text{--S--R}^1\]

- m is an integer from 0 to 50;

- n is an integer from 1 to 60;

- p is an integer from 2 to 6;

- B represents a core of a z-valent, vinyl-terminated polyfunctionalizing agent B(\([-\text{V}--\) \text{]} \text{n} \text{--S--R}^1\]

- \(x\) is an integer from 3 to 6; and

- each V is a group comprising a terminal vinyl group; and each \(-\text{V}--\) is derived from the reaction of \(-\text{V}--\) with a thiol.

In certain embodiments, Formula (4) and in Formula (4a), R\(^3\) is \([--\text{CHR}^3--\text{O}--\text{CHR}^3--\text{]} \text{n} \text{--S--R}^1\]

where \(p\) is 2, X is \(-\text{O}--\), \(q\) is 2, \(r\) is 2, R\(^3\) is ethanediyl, m is 2, and \(n\) is 9.

In certain embodiments of Formula (4) and Formula (4a), R\(^1\) is selected from C\(_{2-5}\) alkanediyl and \([--\text{CHR}^3--\text{O}--\text{CHR}^3--\text{]} \text{n} \text{--S--R}^1\]

In certain embodiments of Formula (4) and Formula (4a), R\(^1\) is \([--\text{CHR}^3--\text{O}--\text{CHR}^3--\text{]} \text{n} \text{--S--R}^1\]

and in certain embodiments X is \(-\text{O}--\) and in certain embodiments, X is \(-\text{S}--\)

In certain embodiments of Formula (4) and Formula (4a), where R\(^3\) is \([--\text{CHR}^3--\text{O}--\text{CHR}^3--\text{]} \text{n} \text{--S--R}^1\]

where \(p\) is 2, \(r\) is 2, \(q\) is 1, and X is \(-\text{S}--\); in certain embodiments, wherein \(p\) is 2, \(q\) is 2, \(r\) is 2, \(X\) is \(-\text{O}--\); and in certain embodiments, \(p\) is 2, \(r\) is 2, \(q\) is 1, and X is \(-\text{O}--\)

In certain embodiments of Formula (4) and Formula (4a), where R\(^1\) is \([--\text{CHR}^3--\text{O}--\text{CHR}^3--\text{]} \text{n} \text{--S--R}^1\]

R\(^1\) is hydrogen, and in certain embodiments, at least one R\(^1\) is methyl.

In certain embodiments of Formula (4) and Formula (4a), each R\(^1\) is the same, and in certain embodiments, at least one R\(^1\) is different.

Various methods can be used to prepare such polyhydrothiols. Examples of suitable thiol-functional polyhydrothiols, and methods for their production, are described in U.S. Pat. No. 6,172,179 at col. 2, line 29 to col. 4, line 22; col. 6, line 39 to col. 10, line 50; and col. 11, lines 65 to col. 12, line 22, the cited portions of which are incorporated herein by reference. Such thiol-functional polyhydrothiols may be difunctional, that is, linear polymers having two thiol terminal groups, or multifunctional, that is, branched polymers having three or more thiol terminal groups. Suitably thiol-functional polyhydrothiols are commercially available, for example, as Permapol® P3.1E, from PRC-Desoto International Inc., Sylmar, Calif.

Suitable thiol-functional polyhydrothiols may be produced by reacting a dienyl ether or mixtures of dienyl ethers with an excess of diethox or a mixture of diethoxehos. For example, diethoxehos suitable for use in preparing thiol-functional polyhydrothiols include those having Formula (5), other diethoxehos disclosed herein, or combinations of any of the diethoxehos disclosed herein.

In certain embodiments, a diethoxeho has the structure of Formula (5):
each X is independently selected from —O—, —S—, and —NR— wherein R is selected from hydrogen and methyl;

s is an integer from 2 to 6;

q is an integer from 1 to 5; and

r is an integer from 2 to 10.

In certain embodiments of a diol of Formula (5), R¹ is \( -(\text{CHR})_2- X - \text{L} \_p \text{L} \_q -(\text{CHR})_2- \).

In certain embodiments of a compound of Formula (5), X is selected from —O— and —S—, and thus \( -(\text{CHR})_2- X - \text{L} \_p \text{L} \_q -(\text{CHR})_2- \), in Formula (5) is \( -(\text{CHR})_2- X - \text{L} \_p \text{L} \_q -(\text{CHR})_2- \), or \( -(\text{CHR})_2- X - \text{L} \_p \text{L} \_q -(\text{CHR})_2- \).

In certain embodiments, p and q are equal, such as where p and q are both two.

In certain embodiments of a diol of Formula (5), R¹ is selected from C₅₋₆ alkanediyl and \( -(\text{CHR})_2- X - \text{L} \_p \text{L} \_q -(\text{CHR})_2- \), and in certain embodiments, X is —O—, and in certain embodiments, X is —S—.

In certain embodiments where R¹ is \( -(\text{CHR})_2- X - \text{L} \_p \text{L} \_q -(\text{CHR})_2- \), p is 2, r is 2, q is 1, and X is —S—, in certain embodiments, wherein p is 2, q is 2, r is 2, and X is —O—, and in certain embodiments, p is 2, r is 2, q is 1, and X is —O—.

In certain embodiments where R¹ is \( -(\text{CHR})_2- X - \text{L} \_p \text{L} \_q -(\text{CHR})_2- \), each R² is hydrogen, and in certain embodiments, at least one R² is methyl.

Examples of suitable diols include, for example, 1,2-ethanediol, 1,2-propanediol, 1,3-propanediol, 1,3-butanediol, 1,4-butanediol, 2,3-butanediol, 1,3-pentanediol, 1,5-pentanediol, 1,6-hexanediol, 1,3-dimercapto-3-methylbutane, dipentene, dimercapto, ethylene glycol diol (ECHDT), dimercaptoethyldisulfide, methyl substituted dimercaptdisulfide, dimethyl substituted dimercaptoethyldisulfide, dimercaptodioxoanione, 1,5-dimercapto-5-oxapentane, and a combination of any of the foregoing. A polyol may have one or more pendant groups selected from a lower (e.g., C₁₋₆) alkyl group, a lower alkoyx group, and a hydroxy group. Suitable alkoyl pendant groups include, for example, C₁₋₆ linear alkoyl, C₅₋₆ branched alkoyl, cyclohexyloxy, and cyclohexyl.

Other examples of suitable diols include dimercapto-dithiol (DMDS) (in Formula (5), R¹ is \( -(\text{CH}_2)_{2p} - X - \text{L} \_p \text{L} \_q -(\text{CH}_2)_{2q} \)), wherein p is 2, r is 2, q is 1, and X is —S—; dimercaptoanione (DMDO) (in Formula (5), R¹ is \( -(\text{CH}_2)_{2p} - X - \text{L} \_p \text{L} \_q -(\text{CH}_2)_{2q} \)), wherein p is 2, q is 2, r is 2, and X is —O—; and 1,5-dimercapto-5-oxapentane (in Formula (5), R¹ is \( -(\text{CH}_2)_{2p} - X - \text{L} \_p \text{L} \_q -(\text{CH}_2)_{2q} \)), wherein p is 2, r is 2, q is 1, and X is —O—. It is also possible to use diolys that include both heteroatoms in the carbon backbone and pendant alkoyl groups, such as methyl groups. Such compounds include, for example, methyl substituted DMDS, such as CH₂—CH(CH₃)₂—S—CH(CH₃)₂—SH, CH₂—CH(CH₃)₂—S—CH₂—SH and dimethyl substituted DMDS, such as CH₂—CH₂CH₂—S—CH₂—CH₂—SH and CH₂—CH₂CH₂—S—CH₂—CH₂—SH.

Suitable divinyl ethers for preparing polythioethers and polythioether adducts include, for example, divinyl ethers of Formula (6):

\[ \text{CH}_2—\text{CH}—\text{O—(R}^2—\text{O—)}_p—\text{CH}—\text{CH}_2 \]

where R² in Formula (6) is selected from a C₅₋₆ n-alkanediyl group, a C₅₋₆ branched alkanediyl group, a C₆₋₈ cycloalkanediyl group, a C₁₀ alkanecycloalkanediyl group, and \( -(\text{CH}_2)_p—\text{O—)}_q—\text{CH}—\text{CH}_2—\) wherein p is an integer ranging from 2 to 6, q is an integer from 1 to 5, and r is an integer from 2 to 10. In certain embodiments of a divinyl ether of Formula (6), R² is a C₅₋₆ n-alkanediyl group, a C₅₋₆ branched alkanediyl group, a C₆₋₈ cycloalkanediyl group, a C₁₀ alkanecycloalkanediyl group, and in certain embodiments, \( -(\text{CH}_2)_p—\text{O—)}_q—\text{CH}—\text{CH}_2—\) is a divinyl ether, for example, diols of Formula (5) or a mixture of at least two different diols of Formula (5), are reacted with a divinyl ether of Formula (6) or a mixture of at least two different divinyl ethers having at least one oxalkanediyl group, such as from 1 to 4 oxalkanediyl groups, i.e., compounds in which m in Formula (6) is an integer ranging from 1 to 4. In certain embodiments, m in Formula (6) is an integer ranging from 2 to 4. It is also possible to employ commercially available divinyl ether mixtures that are characterized by a non-integral average value for the number of oxalkanediyl units per molecule. Thus, n in Formula (6) can also take on rational number values ranging from 0 to 10.0, such as from 1.0 to 10.0, from 1.0 to 4.0, or from 2.0 to 4.0.

Examples of suitable divinyl ethers include, for example, divinyl ether, ethylene glycol divinyl ether (EG-DVE) (R² in Formula (6) is ethanediyl and m is 1), butanediol divinyl ether (BD-DVE) (R² in Formula (6) is butanediyl and m is 1), hexanediol divinyl ether (HD-DVE) (R² in Formula (6) is hexanediyl and m is 1), diethylene glycol divinyl ether (DEG-DVE) (R² in Formula (6) is ethanediyl and m is 2), triethylene glycol divinyl ether (R² in Formula (14) is ethanediyl and m is 3), tetraethylene glycol divinyl ether (R² in Formula (6) is ethanediyl and m is 4), cyclohexanedimethanol divinyl ether, polytetrahydrofurfuryl divinyl ether, trivinyl ether monomers, such as trimethylolpropane trivinyl ether; tetrafunctional ether monomers, such as pentaerythritol tetravinyl ether; and combinations of two or more such polyvinyl ether monomers. A polyvinyl ether may have one or more pendant groups selected from alkoyl groups, hydroxyl groups, alkoxy groups, and amine groups. In certain embodiments, divinyl ethers in which R² in Formula (6) is C₅₋₆ branched alkanediyl may be prepared by reacting a polyhydroxy compound with acetylene. Examples of divinyl ethers of this type include compounds in which R² in Formula (6) is an alkyl-substituted methanediyl group such as —CH(CH₃)₂— (for example Pluronic® blends such as Pluronic® E-200 divinyl ether (BASF Corp., Parsippany, N.J.), for which R² in Formula (6) is ethanediyl and m is 3.8) or an alkyl-substituted ethanediyl (for example CH₂—CH(CH₃)₂— such as DPE polymerics blends including DPE-2 and DPE-3 (International Specialty Products, Wayne, N.J.)).

Other useful divinyl ethers include compounds in which R² in Formula (6) is polytetrahydrofurfuryl (poly-THF) or polyoxyalkanediyl, such as those having an average of about 3 monomer units. Two or more types of polyvinyl ether monomers of Formula (6) may be used. Thus, in certain embodiments, two diols of Formula (5) and one polyvinyl ether monomer of Formula (6), one diol of Formula (5) and two polyvinyl ether monomers of Formula (6), two diols of Formula (5) and two divinyl ether monomers of Formula (6), and more than two compounds of one or both Formula (5) and Formula (6), may be used to produce a variety of thiol-functional polythioethers.

In certain embodiments, a polyvinyl ether monomer comprises 20 to less than 50 mole percent of the reactants used to prepare a thiol-functional polythioether, and in certain embodiments, 30 to less than 50 mole percent.

In certain embodiments provided by the present disclosure, relative amounts of diols and divinyl ethers are selected to yield polythioethers having terminal thiol groups. Thus, a diol of Formula (5) or a mixture of at least two different diols of Formula (5), are reacted with a divinyl ether of Formula (6) or a mixture of at least two different divinyl ethers.
ethers of Formula (6) in relative amounts such that the molar ratio of thiol groups to vinyl groups is greater than 1:1, such as 1.1 to 2.0:1.0.

The reaction between compounds of diols and divinyl ethers may be catalyzed by a free-radical catalyst. Suitable free-radical catalysts include, for example, azo compounds, for example azobisisobutyronitrile (AIBN); organic peroxides such as benzoyl peroxide and t-butyl peroxide; and inorganic peroxides such as hydrogen peroxide. The catalyst may be a free-radical catalyst, an ionic catalyst, or ultraviolet radiation. In certain embodiments, the catalyst does not comprise acidic or basic compounds, and does not produce acidic or basic compounds upon decomposition. Examples of free-radical catalysts include azo-type catalyst, such as Vazo®-57 (Du Pont); Vazo®-64 (Du Pont); Vazo®-67 (Du Pont); V-70® (Wako Specialty Chemicals); and V-65® (Wako Specialty Chemicals). Examples of other free-radical catalysts are alkyl peroxides, such as t-butyl peroxide. The reaction may also be affected by irradiation with ultraviolet light either with or without a cationic photoinitiating moiety.

Thiol-functional polythioethers provided by the present disclosure may be prepared by combining at least one compound of Formula (5) and at least one compound of Formula (6) followed by addition of an appropriate catalyst, and carrying out the reaction at a temperature from 30°C to 120°C, such as 70°C to 90°C, for a time from 2 to 24 hours, such as 2 to 6 hours.

As disclosed herein, thiol-terminated polythioethers may comprise a polyfunctional polythioether, i.e., may have an average functionality of greater than 2.0. Suitable polyfunctional-thiol-terminated polythioethers include, for example, those having the structure of Formula (7):

\[ B-(A-SH)_{2} \]

wherein: (i) A comprises, for example, a structure of Formula (1), (ii) B denotes a z-valent residue of a polyfunctionalizing agent; and (iii) z has an average value of greater than 2.0, and, in certain embodiments, a value between 2 and 3, a value between 2 and 4, a value between 3 and 6, and in certain embodiments, is an integer from 3 to 6.

Polyfunctionalizing agents suitable for use in preparing such polyfunctional thiol-functional polymers include trifunctionalizing agents, that is, compounds where z is 3. Suitable trifunctionalizing agents include, for example, triallyl cyanurate (TAC), 1,2,3-propanetriol, isocyanurates-containing triethanol, and combinations thereof, as disclosed in U.S. Publication No. 2010/0011033 at paragraphs [0102]-[0105], the cited portion of which is incorporated herein by reference. Other useful polyfunctionalizing agents include trimethylpropane trivinyl ether, and the polythioaldehydes described in U.S. Pat. Nos. 4,366,307; 4,605,762; and 5,225,472. Mixtures of polyfunctionalizing agents may also be used.

As a result, thiol-functional polythioethers suitable for use in embodiments provided by the present disclosure may have a wide range of average functionality. For example, trifunctionalizing agents may afford average functionalities from 2.05 to 3.0, such as from 2.1 to 2.6. Wider ranges of average functionality may be achieved by using tetrafunctional or higher functionality polyfunctionalizing agents. Functionality may also be affected by factors such as stoichiometry, as will be understood by those skilled in the art.

Thiol-functional polythioethers having a functionality greater than 2.0 may be prepared in a manner similar to the difunctional thiol-functional polythioethers described in U.S. Publication No. 2010/0011033. In certain embodiments, polythioethers may be prepared by combining (i) one or more dithiols described herein, with (ii) one or more divinyl ethers described herein, and (iii) one or more polyfunctionalizing agents. The mixture may then be reacted, optionally in the presence of a suitable catalyst, to afford a thiol-functional polythioether having a functionality greater than 2.0.

Thus, in certain embodiments, a thiol-terminated polythioether comprises the reaction product of reactants comprising:

(a) a diol of Formula (5):

\[ R_{3}-S-H \]

wherein:

- R is selected from C₂₋₆ alkane, C₆₋₈ cycloalkane, C₆₋₁₃ alkyl/heterocycle, and [-(-CHR)ⁿ₋₁ -X-]ₙ(-CHR)ⁿ₋₁, wherein each R is independently selected from hydrogen and methyl;
- X is independently selected from O, S, —NH—, and —NR— wherein R is selected from hydrogen and methyl;
- s is an integer from 2 to 6;
- q is an integer from 1 to 5; and
- r is an integer from 2 to 10.

(b) a divinyl ether of Formula (6):

\[ CH={C}_{O}(-R^{2}O-),CH={C}_{O}(-R^{2}O-),CH={C}_{O}(-R^{2}O-),CH={C}_{O}(-R^{2}O-) \]

wherein:

- each R² is independently selected from C₁₋₁₀ alkane, C₆₋₈ cycloalkane, C₆₋₁₄ alkyl/heterocycle, and [-(-CHR)ⁿ₋₁ -X-]ₙ(-CHR)ⁿ₋₁, wherein s, q, r, R², and X are as defined above;
- m is an integer from 0 to 50;
- n is an integer from 1 to 60; and
- p is an integer from 2 to 6.

And, in certain embodiments, the reactants comprise (c) a polyfunctional compound such as a polyfunctional compound B(V), wherein B, —V, and z are as defined herein.

Thiol-terminated polythioethers provided by the present disclosure represent thiol-terminated polythioethers having a molecular weight distribution. In certain embodiments, useful thiol-terminated polythioethers can exhibit a number average molecular weight ranging from 500 Daltons to 20,000 Daltons, in certain embodiments, from 2,000 Daltons to 5,000 Daltons, and in certain embodiments, from 3,000 Daltons to 4,000 Daltons. In certain embodiments, useful thiol-terminated polythioethers exhibit a polydispersity (Mw/Mn; weight average molecular weight/number average molecular weight) ranging from 1 to 20, and in certain embodiments, from 1 to 5. The molecular weight distribution of thiol-terminated polythioethers may be characterized by gel permeation chromatography.

In certain embodiments, thiol-functional polythioethers provided by the present disclosure are essentially free, or free, of sulfone, ester and/or disulfide linkages. As used herein, “essentially free of sulfone, ester, and/or disulfide linkages” means that less than 2 mole percent of the linkages in the thiol-functional polymer are sulfone, ester, and/or disulfide linkages. As a result, in certain embodiments, the resulting thiol-functional polythioethers are also essentially free, or free, of sulfone, ester, and/or disulfide linkages.

To prepare a sulfur-containing Michael acceptor adduct, a sulfur-containing polymer such as those disclosed herein may be reacted with (b) a compound having a group that is reactive with the terminal groups of the sulfur-containing polymer and a Michael acceptor group.
In certain embodiments, a Michael acceptor group is
selected from a vinyl ketone, a vinyl sulfone, a quinone, an
aldehyde, a ketone, a vinyl sulfone, and an oxazolidine.
In certain embodiments, a Michael acceptor group is a vinyl
ketone, and in certain embodiments, a vinyl sulfone such as
divinyl sulfone. In embodiments in which the compound
having a Michael acceptor group is divinyl sulfone, the sul-
fur-containing polymer may be thiol-terminated such as a
thiol-terminated polythioether, a thiol-terminated polysul-
fide, or a combination thereof.

The reaction between a sulfur-containing polymer and a
compound having a Michael acceptor group and a group that
is reactive with a terminal group of the sulfur-containing
polymer can be performed in the presence of an appropriate
catalyst. For example, in embodiments in which the sulfur-con-
taining polymer is thiol-terminated and the compound is a
difunctional Michael acceptor, the reaction may take place in
the presence of an amine catalyst. Examples of suitable amine
catalysts include, for example, triethylenediamine, bis-
(2-dimethylaminoethyl) ether, N-ethylmorpholine, triethylen,
1,8-diaza-bicyclo[2.2.2]octane, DABCO, dimethylcyclohexylamine
(DMCHA), dimethylethanolamine (DMEA), bis-
(2-dimethylaminomethyl)ether, N-ethylmorpholine, triethylen,
1,8-diazabicyclo[5.4.0]undecene-7 (DBU), pentamethylene
dimethyletheramine (PMDETA), benzylidimethylamine
(BDMA), N,N,N-trimethyl-N′-hydroxyethyl-bis(aminometh-
ylether), and N-(3-diethylamino)propyl-N,N-dimethyl-
1,3-propanediamine.

Compositions

Michael addition chemistries may be employed in a variety
of ways in conjunction with sulfur-containing polymers to
provide curable compositions. For example, a curable com-
position provided by the present disclosure may comprise (a)
a sulfur-containing polymer and a Michael acceptor curing
agent; (b) a sulfur-containing Michael acceptor adduct and a
curing agent comprising at least two terminal groups that are
reactive with Michael acceptor groups; or (c) a sulfur-con-
taining polymer and a curing agent comprising a combina-
tion of a monomeric Michael acceptor and a sulfur-containing
Michael acceptor adduct.

Sulfur-Containing Polymer and Michael Acceptor
Curing Agent

In certain embodiments, compositions provided by the
present disclosure comprise a sulfur-containing polymer and a
Michael acceptor curing agent. A sulfur-containing polymer
may be a polythioether or combination of polythioethers hav-
ing terminal groups reactive with the Michael acceptor; a
polysulfide or combination of polysulfides having terminal
groups reactive with the Michael acceptor; or a combination
of any of the foregoing. In certain embodiments, a sulfur-
containing polymer is thiol-terminated. In such embodi-
ments, a Michael acceptor will be polyfunctional and have
Michael acceptor groups reactive with the terminal groups of
the sulfur-containing polymer.

In certain embodiments, a sulfur-containing polymer com-
prises a thiol-terminated polythioether, including any of the
thiol-terminated polythioethers disclosed herein, such as a
thiol-terminated polythioether of Formula (1). In certain embodi-
ments, a sulfur-containing polymer comprises a thiol-
terminated polythioether, such as a thiol-terminated polythio-
ether of Formula (4), Formula (4a), or a combination thereof.

In certain embodiments, a sulfur-containing polymer is
selected from a difunctional sulfur-containing polymer, a tri-
functional-containing polymer and a combination of thereof.

In certain embodiments, a thiol-terminated polymer com-
prises a mixture of sulfur-containing polymers having an
average functionality from 2 to 3, and in certain embodi-
ments, from 2.2 to 2.8. In certain embodiments, a thiol-ter-
minal polythioether comprises Permap® 3.1E, available from
PRC-DeSoto International.

A polyfunctional Michael acceptor has at least two
Michael acceptor groups. A polyfunctional Michael acceptor
can have an average Michael acceptor functionality from 2 to
6, from 2 to 4, from 2 to 3, and in certain embodiments, from
2.05 to 2.5. In certain embodiments, a polyfunctional Michael
acceptor is difunctional, such as, divinyl ketone and divinyl
sulfone. A Michael acceptor having a functionality greater
than two may be prepared by reacting a compound having a
Michael acceptor group and a group reactive with terminal
groups of a polyfunctionalizing agent such as those disclosed
herein, using appropriate reaction conditions.

In certain embodiments where a Michael acceptor is used
as a curing agent, the molecular weight of the Michael accep-
tor is less than 600 Daltons, less than 400 Daltons, and in
certain embodiments, less than 200 Daltons.

In certain embodiments, a Michael acceptor comprises from
about 0.5 wt % to about 20 wt % of the composition, from
about 1 wt % to about 10 wt %, from about 2 wt % to about
8 wt %, from about 2 wt % to about 6 wt %, and in
certain embodiments, from about 3 wt % to about 5 wt %,
where wt % is based on the total dry solids weight of the
composition.

Sulfur-Containing Michael Acceptor Adduct and a
Curing Agent

In certain embodiments, a composition comprises a sulfur-
containing Michael acceptor adduct provided by the present
disclosure and a sulfur-containing polymer curing agent.

In such compositions a sulfur-containing adduct comprises
any of those disclosed herein. In certain embodiments, a sulfur-containing adduct comprises a polythioether adduct,
and in certain embodiments a polythioether adduct has an
average functionality from 2 to 3, from 2.2 to 2.8, and in
certain embodiments, from 2.4 to 2.6. In certain embodi-
ments, a sulfur-containing adduct has an average func-

tionality of 2.

In certain embodiments, a sulfur-containing Michael
acceptor adduct comprises a compound of Formula (3), Form-
ula (3a), or a combination thereof, and the sulfur-containing
polymer curing agent comprises a polythioether of Formula
(4), Formula (4a), or a combination thereof. In certain embodi-
ments, the sulfur-containing adduct comprises the
Michael acceptor adduct of Permap® 3.1E. In certain embodi-
ments, the sulfur-containing polymer curing agent

compares Permap® 3.1E.

In certain embodiments, a sulfur-containing Michael
acceptor adduct comprises a compound of Formula (3), Form-
ula (3a), or a combination thereof, and the sulfur-containing
polymer curing agent comprises a polysulfide. In certain embodi-
ments, the sulfur-containing adduct comprises the
Michael acceptor adduct of Permap® 3.1E. In certain embodi-
ments, the sulfur-containing polymer comprises a polysulfide
selected from a Thiokol-LP®, polysulfide, a Thiokol®
polysulfide, and a combination thereof.

In such compositions the Michael acceptor groups of the
adduct are reactive with the terminal groups of the sulfur-
containing polymer. For example, the Michael acceptor
groups may be activated alkyl groups, e.g., Michael acceptor groups, and the sulfur-containing polymer comprises terminal thiol groups.

A sulfur-containing polymer used as a curing agent comprises at least two terminal groups reactive with Michael acceptor groups. A sulfur-containing polymer used as a curing agent in such compositions may comprise a polythioether including any of those disclosed herein, a polysulfide including any of those disclosed herein, or a combination thereof. The sulfur-containing polymer may have an average functionality of about 2 or any functionality from about 2 and about 6, such as from about 2 to about 4, or from about 2 to about 3.

In certain embodiments, the sulfur-containing polymer curing agent comprises a thiol-terminated polythioether such as, for example, Permapol® 3,1E. In certain embodiments, the sulfur-containing polymer comprises a thiol-terminated polysulfide such as, for example, a Thiokol-L-P® polysulfide, a Thioplast® polysulfide, or a combination thereof.

In such embodiments, when used as a curing agent, a sulfur-containing polymer, comprises from about 20 wt % to about 90 wt % of the composition, from about 30 wt % to about 80 wt %, from about 40 wt % to about 60 wt %, and in certain embodiments, about 50 wt %, where wt % is based on the total dry weight of the composition.

In such embodiments, a sulfur-containing Michael acceptor adduct comprises from about 20 wt % to about 90 wt % of the composition, from about 30 wt % to about 80 wt %, from about 40 wt % to about 60 wt %, and in certain embodiments, about 50 wt %, where wt % is based on the total dry weight of the composition.

Compositions comprising a sulfur-containing Michael acceptor adduct and a sulfur-containing polymer curing agent may comprise a catalyst such as an amine catalyst including any of those disclosed herein.

In certain embodiments, a composition comprises a polythioether adduct and a curing agent. A polythioether adduct includes any of those disclosed herein, such as polythioether adducts of Formula (3), Formula (3a), and combinations thereof.

In certain embodiments of such compositions, the composition comprises a sulfur-containing Michael acceptor adduct provided by the present disclosure and a curing agent selected from a sulfur-containing polymer comprising at least two terminal groups reactive with Michael acceptor groups, a monomeric thiol, a polythiol, a polyamine, a blocked polyamine, and a combination of any of the foregoing. In certain embodiments, a curing agent comprises a sulfur-containing polymer comprising at least two terminal groups reactive with Michael acceptor groups; in certain embodiments a monomeric thiol; in certain embodiments a polythiol; in certain embodiments a polyamine; and in certain embodiments, a blocked polyamine. In certain embodiments of such compositions, a curing agent comprises a sulfur-containing polymer comprising at least two terminal groups reactive with Michael acceptor groups and a compound having at least two terminal groups reactive with Michael acceptor groups selected from a monomeric thiol, a polythiol, a polyamine, a blocked polyamine, and a combination of any of the foregoing.

In certain embodiments, a sulfur-containing polymer comprising at least two terminal groups reactive with Michael acceptor groups is selected from a polythioether polymer comprising at least two terminal groups reactive with Michael acceptor groups, a polysulfide polymer comprising at least two terminal groups reactive with Michael acceptor groups, and a combination thereof. In certain embodiments, the terminal groups reactive with Michael acceptor groups are terminal thiol groups. In such embodiments, a thiol-terminated polythioether may be selected from a polythioether of Formula (4), a polythioether of Formula (4a), and a combination thereof. In certain embodiments, the sulfur-containing polymer curing agent comprises a thiol-terminated polysulfide such as, for example, Thiokol-L-P® and Thioplast® polysulfide polymers.

In certain compositions, the curing agent comprises a monomeric thiol. A monomeric thiol refers to a compound having at least two terminal thiol groups. Examples of monomeric thiols include dithiols of Formula (5). Polythiols refer to higher molecular weight compounds having terminal thiol groups and thiol groups in the backbone.

Examples of polyamines include, for example, aliphatic polyamines, cycloaliphatic polyamines, aromatic polyamines and mixtures thereof. In certain embodiments, the polyamine can include a polyamine having at least two functional groups independently chosen from primary amine (—NH₂), secondary amine (—NH—) and combinations thereof. In certain embodiments, the polyamine has at least two primary amine groups.

In certain embodiments, a polyamine is a sulfur-containing polyamine. Examples of suitable sulfur-containing polyamines are isomers of benzenediamine-bis(methylthio), such as 1,3-benzenediamine-4-methyl-2,6-bis(methylthio)- and 1,3-benzenediamine-2-methyl-4,6-bis(methylthio), having the structure:

```
CH₃S
H
\------\------
     |       |
SCH₃ | NH₂ |
\------\------
     |       |
    CH₃     |
```

Such sulfur-containing polyamines are commercially available, for example, from Albemarle Corporation under the tradename Ethacure® 300. Suitable polyamines also include, for example, polyamines having the following structure:

```
H₂N
R₁²
\------\------
     |       |
R₂¹ | R₁¹ |
\------\------
     |       |
R₁⁻¹ R₂⁻¹
```

wherein each R₁¹ and each R₂¹ are independently selected from methyl, ethyl, propyl, and isopropyl groups, and each R₁⁻¹ is independently selected from hydrogen and chlorine. Examples of suitable amine-containing curing agents include the following compounds available from Lonza Ltd. (Bosel, Switzerland): Lonza® M-DIPA, Lonza® M-DMA, Lonza® M-MEA, Lonza® M-DEA, Lonza® M-MIPA, Lonza® M-MDEA, Lonza® M-CDEA.

In certain embodiments, a polyamine comprises a diamine, such as 4,4’-methylenebis(3-chloro-2,6-diethylaniline) (Lonza® M-CDEA), 2,4-diamino-3,5-diethyl-toluene, 2,6-diamino-3,5-diethyl-toluene and mixtures thereof (col-
llectively diethyltoluenediamine or DETDA), a sulfur-con-
taining diamine, such as Etecure® 300, 4,4'-methylene-bis-
(2-chloroaniline) and mixtures thereof. Other suitable
diamines include 4,4'-methylene-bis(dialkylaniline), 4,4'-
methylene-bis(2,6-diisopropylaniline), 4,4'-
methylene-bis(2,6-diisopropylaniline), 4,4'-
methylene-bis(2,6-diethyl-6-methyl-
aniline), and combinations of any of the foregoing.

Further, examples of suitable polyamines include ethyl-
enediamine, such as, ethylenediamine (EDA), diethylenetri-
amine (DETA), triethylenetetramine (TETA), tetraethylen-
epentamine (TEPA), pentaethylenehexamine (PEHA),
iperazine, morpholine, substituted morpholine, piperidine,
substituted piperidine, diethylenediamine (DEEDA), 2-amino-
1-ethylpiperazene, and combinations thereof. In certain
embodiments, a polyamine may be selected from one or more
isomers of C_{13}, dialkyl toluidenediamine, such as, 3,5-dim-
ethyl-2,4-toluidenediamine, 3,5-dimethyl-2,6-toluidenediamine,
3,5-diethyl-2,4-toluidenediamine, 3,5-diethyl-2,6-toluidenedi-
amine, 3,5-diisopropyl-2,4-toluidenediamine, 3,5-diisopropyl-
2,6-toluidenediamine, and combinations thereof. In certain
embodiments, a polyamine may be selected from methylene
dianiline, trimethylene glycol di( para-amino benzolate), and
combinations thereof.

In certain embodiments, a polyamine includes a compound
having the structure:

```
  H2N  
  /    
  /     
N2H  
|     
|     
  H2N  or 
  /    
  /     
N2H  
|     
|     
  H2N  
  /    
  /     
N2H  
```

In certain embodiments, a polyamine includes one or more
methylene bis anilines, one or more aniline sulfides, and/or
one or more biaminated polyamines that may be represented by the general
structures disclosed, for example, in paragraph [0072] of
U.S. Patent No. 2011/0092639, which is incorporated by reference herein.

In certain embodiments, a polyamine includes compounds represented by the general structure:

```
  R20
  /    
  /     
N2H  
|     
|     
  R21  
  /    
  /     
N2H  
|     
|     
  R22  
  /    
  /     
N2H  
```

where R^{20}, R^{21}, R^{22}, and R^{23} are independently selected from
C_{13}, alkyl, CH_{3} — and halogen, such as but not limited to
chlorine or bromine. In certain embodiments, a polyamine
represented by the immediately preceding structure may be
diethyl toluene diamine (DETDMA) wherein R^{23} is methyl, R^{20}
and R^{21} are each ethyl, and R^{22} is hydrogen. In certain
embodiments, the polyamine is 4,4'-methyleneedianiline.

Examples of blocked polyamines include ketimines,
enamines, oxazolidines, aldazines, and imidazolidines. In
certain embodiments, the blocked polyamine is Vestamin® A
139.

Sulfur-Containing Polymer Adduct,
Sulfur-Containing Polymer, and a Compound
Having at Least Two Michael Acceptor Groups

In certain embodiments, a composition comprises a sulfur-
containing polymer, and a sulfur-containing Michael accep-
tor adduct. In certain embodiments, a composition comprises
a sulfur-containing polymer, a polyfunctional Michael accep-
tor, and a sulfur-containing Michael acceptor adduct.

In such compositions, a sulfur-containing polymer com-
prises at least two terminal groups reactive with Michael
acceptor groups. In such compositions, the sulfur-containing
polymer may be selected from a polythioether polymer, a
polysulfide polymer, or a combination thereof, including a
suitable polythioether polymer or polysulfide polymer pro-
vided by the present disclosure.

In certain embodiments, a sulfur-containing polymer is
selected such that the terminal groups are reactive with the
polyfunctional Michael acceptor and the sulfur-containing
Michael acceptor adduct. In certain embodiments, a sulfur-
containing polymer comprises terminal thiol groups includ-
ing any of the thiol-terminated polythioethers, thiol-termin-
ated polysulfides, and combinations thereof disclosed
herein.

In certain embodiments of such compositions, a sulfur-
containing polymer adduct comprises a polythioether poly-
mer adduct provided by the present disclosure, a polysulfide
polymer adduct provided by the present disclosure, or a com-
ination thereof.

When a composition comprises a polyfunctional mono-
meric Michael acceptor, any suitable monomeric Michael
acceptor having at least two Michael acceptor groups such as,
for example, divinyl sulfone or other Michael acceptors
including any of those disclosed herein may be used.

In certain embodiments, a sulfur-containing polymer is
selected from a polythioether of Formula (3), Formula (3a),
and a combination thereof; a polyfunctional Michael acceptor
adduct is selected from an adduct of Formula (4), Formula
(4a), and a combination thereof; and a polyfunctional mono-
meric Michael acceptor is selected from a compound having
two or more activated alkenyl groups such as a vinylketone or
a vinyl sulfone, such as divinyl sulfone.

In such embodiments, the polyfunctional Michael acceptor
and Michael acceptor adduct comprise 10 wt % to 90 wt % of
the composition, from 20 wt % to 80 wt %, from 30 wt % to
70 wt %, and in certain embodiments, from 40 wt % to 60 wt
%, where wt % is based on the total dry solids weight of the
composition.

Compositions comprising a sulfur-containing polymer, a
polyfunctional Michael acceptor, and a sulfur-containing
polymer adduct may comprise a catalyst such as an amine
catalyst including any of those disclosed herein.

Epoxy Blend

In certain embodiments, compositions provided by the
present disclosure comprise an epoxy curing agent. Thus, in
addition to a Michael acceptor curing agent, a sulfur-contain-
ing polymer curing agent, and/or a sulfur-containing Michael
acceptor adduct curing agent, a composition may comprise
one or more polyepoxy curing agents. Examples of suitable epoxies include, for example, polyepoxide resins such as hydantoin diepoxide, diacyclopentadiene diether of bisphenol-A, diglycidyl ether of bisphenol-F, Novolac® type epoxides such as DENTM 438 (available from Dow), certain epoxidized unsaturated resins, and combinations of any of the foregoing. A polyepoxide refers to a compound having two or more reactive epoxy groups.

In certain embodiments, a polyepoxy curing agent comprises an epoxy-functional polymer. Examples of suitable epoxy-functional polymers include the epoxy-functional polyformal polymers disclosed in U.S. patent application Ser. No. 13/050,988 and epoxy-functional polythioether polymers disclosed in U.S. Pat. No. 7,671,145. In general, when used as a curing agent, an epoxy-functional polymer has a molecular weight less than about 2,000 Daltons, less than about 1,500,000 Daltons, and in certain embodiments, less than about 500 Daltons.

In such compositions, an epoxy may comprise about 0.5 wt % to about 20 wt % of the composition, from about 1 wt % to about 10 wt %, from about 2 wt % to about 8 wt %, from about 2 wt % to about 6 wt %, and in certain embodiments, from about 3 wt % to about 5 wt %, where wt % is based on the total solids weight of the composition.

**Isocyanate Blend**

In certain embodiments, compositions provided by the present disclosure comprise an isocyanate curing agent. Thus, in addition to a Michael acceptor curing agent, a sulfur-containing polymeric curing agent, and/or a sulfur-containing Michael acceptor curing agent, a composition may comprise one or more polyisocyanate curing agents that are reactive with thiol groups but not reactive with Michael acceptor groups such as vinyl sulfone groups. Examples of suitable isocyanate curing agents include aliphatic isocyanate, 3-isopropylisocyanate, α-dimethylbenzyl isocyanate, toluene disocyanate, and combinations of any of the foregoing. Isocyanate curing agents are commercially available and include, for example, products under the tradenames Baydur® (Bayer MaterialScience), Desmodur® (Bayer MaterialScience), Suhbond® (DSM), Ecco® (ECCO), Vestanat® (Evonik), Irodor® (Huntsman), Rhodocord® (Perstorph), and Vanchem® (V.T. Vanderbilt). In certain embodiments, a polyisocyanate curing agent comprises isocyanate groups that are reactive with thiol groups and that are less reactive with Michael acceptor groups.

In certain embodiments, an isocyanate curing agent comprises an isocyanate-functional polymer. Examples of suitable isocyanate-functional polymers include the isocyanate-functional polyformal polymers disclosed in U.S. patent application Ser. No. 13/051,002. In general, when used as a curing agent, an isocyanate-functional polymer has a molecular weight less than about 2,000 Daltons, less than about 1,500,000 Daltons, and in certain embodiments, less than about 500 Daltons.

In such compositions, an epoxy may comprise about 0.5 wt % to about 20 wt % of the composition, from about 1 wt % to about 10 wt %, from about 2 wt % to about 8 wt %, from about 2 wt % to about 6 wt %, and in certain embodiments, from about 3 wt % to about 5 wt % of the composition, where wt % is based on the total solids weight of the composition.

**Hydroxyl and Amine Curing**

Sulfur-containing Michael acceptor adducts provided by the present disclosure may also be modified for use in particular applications and curing chemistries. For example, spray seal applications require rapid curing without heating. Amine-based systems using epoxy curing agents are well suited for such applications. Accordingly, sulfur-containing Michael acceptor adducts may be adapted to other curing chemistries by modifying or capping the terminal Michael acceptor groups with, for example, hydroxyl groups or amine groups.

Hydroxyl-terminated sulfur-containing adducts may be prepared by reacting a sulfur-containing Michael acceptor adduct provided by the present disclosure such as an adduct of Formula (1), Formula (3), or Formula (3a), and a compound having a terminal thiol group and a terminal hydroxyl group. In certain embodiments, a compound having a terminal thiol group and a terminal hydroxyl group has the structure HS—R13—OH, where R13 is selected from C6–8 alkanediyl, C6–8 cycloalkanediyl, C6–10 alkyleneoxyalkanediyl, C6–8 heterocycloalkanediyl, C6–8 arenediyl, C6–10 alkanarediyl, C6–8 hetarediyl, and (—CHR3—)r−X—(—CHR3—)r−, wherein q, r, s, X, and R2 are defined as for Formula (5). In certain embodiments, a sulfur-containing adduct is derived from Permapol-31E. The reaction may take place in the presence of a catalyst at a temperature from about 25° C. to about 50° C.

In certain embodiments, a hydroxyl-terminated sulfur-containing adduct comprises a hydroxyl-terminated polythioether adduct of Formula (8), a hydroxyl-terminated polythioether adduct of Formula (8a), and a combination thereof:

\[
\begin{align*}
R^2_2R^2_-S-R^2_2&\cdots-S-(CH_2)_{r-2}O(=O)-R^2_2-O_{\text{m}}(\text{8}) \\
\text{[R}^2_2R^2_-S-R^2_2&\cdots-S-(CH_2)_{r-2}O(=O)-R^2_2-O_{\text{m}}]_2 \text{(8a)}
\end{align*}
\]

wherein:

- each R1 independently is selected from C6–10 alkanediyl, C6–8 cycloalkanediyl, C6–10 alkyleneoxyalkanediyl, C6–8 heterocycloalkanediyl, and (—CHR3—)r−X—(—CHR3—)r−, wherein q, r, s, X, and R2 are defined as for R12;
- each R2 is independently selected from hydrogen and methyl; and
- each X is independently selected from —O—, —S—, and —NHR—, wherein R is selected from hydrogen and methyl;
- each R2 is independently selected from C6–8 alkanediyl, C6–8 cycloalkanediyl, C6–10 alkyleneoxyalkanediyl, and (—CHR3—)r−X—(—CHR3—)r−, wherein q, r, s, X, and R2 are defined as for R12;
- m is an integer from 0 to 50;
- n is an integer from 1 to 60;
- p is an integer from 2 to 6;
- R represents a core of a z-valent, vinyl-terminated polyfunctionalizing agent (—V—), wherein z is an integer from 3 to 6; and
- each V is a group comprising a terminal vinyl group; each —V— is derived from the reaction of —V with a thiol;
- each —R2 — is (—CH2—C(R)2—SO2—(R)2—CH2—, wherein each R2 is independently selected from hydrogen and C6–10 alkanediyl; and each R2 is moieties having a terminal hydroxyl group. In certain embodiments of Formula (8) and Formula (8a), R2 is selected from —S—R13—OH, wherein R13 is defined as for (5).

In certain embodiments, compositions comprise one or more hydroxyl-terminated sulfur-containing adducts and one
or more polysicyanate curing agents. Examples of suitable isocyanate curing agents include toluene disocyanate, and combinations of any of the foregoing. Isocyanate curing agents are commercially available and include, for example, products under the tradenames Baydur® (Bayer MaterialScience), Desmodur® (Bayer MaterialScience), Bond® (DSM), ECCO (ECCO), Vestanat® (Evonik), Irodur® (Huntsman), Rhodocot™ (Perstorp), and Vanchem® (V.T. Vanderbilt).

Amine-terminated sulfur-containing adducts may be prepared by reacting a sulfur-containing Michael acceptor adduct provided by the present disclosure such as an adduct of Formula (1), (3), or (3a), and a compound having a terminal thiol group and a terminal amine group. In certain embodiments, a compound having a terminal thiol group and a terminal hydroxyl group has the structure H-S-R₁⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻˓  1

In certain embodiments, compositions, combinations comprise one or more amine-terminated sulfur-containing adducts and one or more polysicyanate curing agents such as any of those disclosed herein.

Compositions

Compositions provided by the present disclosure may include one or more catalysts. Catalysts appropriate for use in reactions between Michael acceptors such as activated alkenyl groups and thiil groups include base catalysts such as amines. Examples of suitable amine catalysts include, for example, triethylendiamine (1,4-diazabicyclo[2.2.2]octane, DABCO), dimethylcyclohexylamine (DMCHA), dimethyl-ethanolamine (DMEA), bis-(2-dimethylaminomethyl)ether, N-ethylmorpholine, triethylamine, 1,8-diazabicyclo[5.4.0]undecene-7 (DBU), pentamethyldiethylenetriamine (PMDETA), benzylidimethylamine (BDMBA), N,N',N'-trimethyl-N'-hydroxymethyl-bis(aminomethyl)ether, N,N'-trimethyl(3-dimethylaminopropyl)-N,N-dimethyl-1,3-propanediamine.

In compositions comprising epoxies, the composition may comprise a base catalyst, including amine catalysts such as any of those disclosed herein.

In certain embodiments, compositions provided by the present disclosure comprise one or more than one adhesion promoters. A one or more additional adhesion promoter may be present in amount from 0.1 wt % to 15 wt % of a composition, less than 5 wt %, less than 2 wt %, and in certain embodiments, less than 1 wt %, based on the total dry weight of the composition. Examples of adhesion promoters include phenolics, such as Methylen® phenolic resin, and organosilanes, such as epoxy, mercapto or amino functional silanes, such as Silquest® A-187 and Silquest® A-1100. Other useful adhesion promoters are known in the art.

Compositions provided by the present disclosure may comprise one or more different types of filler. Suitable fillers include those commonly known in the art, including inorganic fillers, such as carbon black and calcium carbonate (CaCO₃), silica, polymer powders, and lightweight fillers. Suitable lightweight fillers include, for example, those described in U.S. Pat. No. 6,525,168. In certain embodiments, a composition includes 5 wt % to 60 wt % of the filler or combination of fillers, 10 wt % to 50 wt %, and in certain embodiments, from 20 wt % to 40 wt %, based on the total dry weight of the composition. Compositions provided by the present disclosure may further include one or more colorants, thixotropic agents, accelerators, fire retardants, adhesion promoters, solvents, masking agents, or a combination of any of the foregoing. As can be appreciated, fillers and additives employed in a composition may be selected so as to be compatible with each other as well as the polymeric component, curing agent, and/or catalyst.

In certain embodiments, compositions provided by the present disclosure include low density filler particles. As used herein, low density, when used with reference to such particles means that the particles have a specific gravity of no more than 0.7, in certain embodiments no more than 0.25, and in certain embodiments, no more than 0.1. Suitable lightweight filler particles often fall within two categories — microspheres and amorphous particles. The specific gravity of microspheres may range from 0.1 to 0.7 and include, for example, polyethylene foam, microspheres of polycrylates and polyolefins, and silica microspheres having particle sizes
ranging from 5 to 100 microns and a specific gravity of 0.25 (Eccospheres®). Other examples include alumina/silica microspheres having particle sizes in the range of 5 to 300 microns and a specific gravity of 0.7 (Filite®, aluminum silicate microspheres having a specific gravity of from about 0.45 to about 0.7 (Z-Light®), calcium carbonate coated polyvinylidene copolymer microspheres having a specific gravity of 0.13 (Duolite® 6001 AE), and calcium carbonate coated acrylonitrile copolymer microspheres such as Duolite® E135, having an average particle size of about 40 μm and a density of 0.135 g/cc (Henkel). Suitable fillers for decreasing the specific gravity of the composition include, for example, hollow microspheres such as Expander® microspheres (available from AkzoNobel) or Duolite® low density polymer microspheres (available from Henkel). In certain embodiments, compositions provided by the present disclosure include lightweight filler particles comprising an exterior surface coated with a thin coating, such as those described in U.S. Publication No. 2010/0041839 at paragraphs [0016]-[0052], the cited portion of which is incorporated herein by reference.

In certain embodiments, a low density filler comprises less than 2 wt % of a composition, less than 1.5 wt %, less than 1.0 wt %, less than 0.8 wt %, less than 0.75 wt %, less than 0.7 wt % and in certain embodiments, less than 0.5 wt % of a composition, where wt % is based on the total dry solids weight of the composition. In certain embodiments, compositions provided by the present disclosure comprise at least one filler that is effective in reducing the specific gravity of the composition. In certain embodiments, the specific gravity of a composition is from 0.8 to 1, 0.7 to 0.9, from 0.75 to 0.85, and in certain embodiments, is 0.8. In certain embodiments, the specific gravity of a composition is less than about 0.9, less than about 0.8, less than about 0.75, less than about 0.7, less than about 0.65, less than about 0.6, and in certain embodiments, less than about 0.55.

In certain embodiments, compositions provided by the present disclosure comprise an electrically conductive filler. Electrical conductivity and EMI/RF shielding effectiveness can be imparted to composition by incorporating conductive materials within the polymer. The conductive elements can include, for example, metal or metal-plated particles, fabrics, meshes, fibers, and combinations thereof. The metal can be in the form of, for example, filaments, particles, flakes, or spheres. Examples of metals include copper, nickel, silver, aluminum, tin, and steel. Other conductive materials that can be used to impart EMI/RF shielding effectiveness to polymer compositions include conductive particles or fibers comprising carbon or graphite. Conductive polymers such as polythiophenes, polypyrroles, polyaniline, poly(p-phenylene) vinylene, polyphenylene sulfide, polyphenylene, and polyacetylene can also be used.

Examples of electrically non-conductive fillers include materials such as, but not limited to, calcium carbonate, mica, polyamide, fumed silica, molecular sieve powder, microspheres, titanium dioxide, chalks, alkali blacks, cellulose, zinc sulfide, heavy spar, alkali earth oxides, alkali earth hydroxides, and the like. Fillers also include high band gap materials such as zinc sulfide and inorganic barium compounds. In certain embodiments, an electrically conductive base composition can comprise an amount of electrically non-conductive filler ranging from 2 wt % to 10 wt % based on the total weight of the base composition, and in certain embodiments, can range from 3 wt % to 7 wt %. In certain embodiments, a curing agent composition can comprise an amount of electrically non-conductive filler ranging from less than 6 wt % and in certain embodiments ranging from 0.5% to 4% by weight, based on the total weight of the curing agent composition.

Fillers used to impart electrical conductivity and EMI/RF shielding effectiveness to polymer compositions are well known in the art. Examples of electrically conductive fillers include electrically conductive noble metal-based fillers such as pure silver; noble metal-plated noble metals such as silver-plated gold; noble metal-plated non-noble metals such as silver plated cooper, nickel or aluminum, for example, silver-plated aluminum core particles or platinum-plated copper particles; noble-metal-plated glass, plastic or ceramics such as silver-plated glass microspheres, noble-metal plated aluminum or noble-metal plated plastic microspheres; noble-metal plated mica; and other such noble-metal conductive fillers. Non-noble metal-based materials can also be used and include, for example, non-noble metal-plated non-noble metals such as copper-coated iron particles or nickel plated copper; non-noble metals, e.g., copper, aluminum, nickel, cobalt; non-noble-metal-plated non-noble metals, e.g., nickel-plated graphite and non-metal materials such as carbon black and graphite. Combinations of electrically conductive fillers can also be used to meet the desired conductivity, EMI/RF shielding effectiveness, hardness, and other properties suitable for a particular application.

The shape and size of the electrically conductive fillers used in the compositions of the present disclosure can be any appropriate shape and size to impart EMI/RF shielding effectiveness to the cured composition. For example, fillers can be of any shape that is generally used in the manufacture of electrically conductive fillers, including spherical, flake, platelet, particle, powder, irregular, fiber, and the like. In certain sealant compositions of the disclosure, a base composition can comprise Ni-coated graphite as a particle, powder or flake. In certain embodiments, the amount of Ni-coated graphite in a base composition can range from 40 wt % to 80 wt %, and in certain embodiments can range from 50 wt % to 70 wt %, based on the total weight of the base composition. In certain embodiments, an electrically conductive filler can comprise Ni fiber. Ni fiber can have a diameter ranging from 10 μm to 50 μm and have a length ranging from 250 μm to 750 μm. A base composition can comprise, for example, an amount of Ni fiber ranging from 2 wt % to 10 wt %, and in certain embodiments, from 4 wt % to 8 wt %, based on the total weight of the base composition.

Carbon fibers, particularly graphitized carbon fibers, can also be used to impart electrical conductivity to compositions of the present disclosure. Carbon fibers formed by vapor phase pyrolysis methods and graphitized by heat treatment and which are hollow or solid with a fiber diameter ranging from 0.1 micron to several microns, have high electrical conductivity. As disclosed in U.S. Pat. No. 6,184,280, carbon microfibers, nanotubes or carbon fibrils having an outer diameter of less than 0.1 μm to tens of nanometers can be used as electrically conductive fillers. An example of graphitized carbon fiber suitable for conductive compositions of the present disclosure include PANEX 30MF (Zoltek Companies, Inc., St. Louis, Mo.), a 0.921 μm diameter round fiber having an electrical resistivity of 0.00055 Ω-cm.

The average particle size of an electrically conductive filler can be within a range useful for imparting electrical conductivity to a polymer-based composition. For example, in certain embodiments, the particle size of the one or more fillers can range from 0.25 μm to 250 μm, in certain embodiments can range from 0.25 μm to 75 μm, and in certain embodiments can range from 0.25 μm to 60 μm. In certain embodiments, composition of the present disclosure can comprise Keltjen
Black EC-600 JD (Akzo Nobel, Inc., Chicago, Ill.), an electrically conductive carbon black characterized by an iodine absorption of 1000-1150 mg/g (30/84-5 test method), and a pore volume of 480-510 cm$^3$/g (DHP adsorption, KTM 81-3504). In certain embodiments, an electrically conductive carbon black filler is Black Pearls 2000 (Cabot Corporation, Boston, Mass.).

In certain embodiments, electrically conductive polymers can be used to impart or modify the electrical conductivity of compositions of the present disclosure. Polymers having sulfur atoms incorporated into aromatic groups or adjacent to double bonds, such as in polyphenylene sulfide, and polynaphthylene, are known to be electrically conductive. Other electrically conductive polymers include, for example, poly-5

pyrroles, polyalanine, poly(phenylene vinylene), and poly-acetylene. In certain embodiments, the sulfur-containing polymers forming a base composition can be polysulfides and/or polythioethers. As such, the sulfur-containing polymers can comprise aromatic sulfur groups and sulfur atoms adjacent to conjugated double bonds such as vinylcyclohexene-dimercurdioxacetylene groups, to enhance the electrical conductivity of the compositions of the present disclosure.

Compositions of the present disclosure can comprise more than one electrically conductive filler and the more than one electrically conductive filler can be of the same or different materials and/or shapes. For example, a sealant composition can comprise electrically conductive Ni fibers, and electrically conductive Ni-coated graphite in the form of powder, particles or flakes. The amount and type of electrically conductive filler can be selected to produce a sealant composition which, when cured, exhibits a sheet resistance (four-point resistance) of less than 0.50 Q/cm$^2$, and in certain embodiments, a sheet resistance less than 0.75 Q/cm$^2$. The amount and type of filler can also be selected to provide effective EMI/RFI shielding over a frequency range of from 1 MHz to 18 GHz for an aperture sealed using a sealant composition of the present disclosure.

Galvanic corrosion of dissimilar metal surfaces and the conductive compositions of the present disclosure can be minimized or prevented by adding corrosion inhibitors to the composition, and/or by selecting appropriate conductive fillers. In certain embodiments, corrosion inhibitors include stannous chromate, calcium chromate, magnesium chromate, and combinations thereof. U.S. Pat. No. 5,284,888 and U.S. Pat. No. 5,270,364 disclose the use of aromatic triazoles to inhibit corrosion of aluminum and steel surfaces. In certain embodiments, a sacrificial oxygen scavenger such as Zn can be used as a corrosion inhibitor. In certain embodiments, the corrosion inhibitor can comprise less than 10% by weight of the total weight of the electrically conductive composition. In certain embodiments, the corrosion inhibitor can comprise an amount ranging from 2% by weight to 8% by weight of the total weight of the electrically conductive composition. Corrosion between dissimilar metal surfaces can also be minimized or prevented by the selection of the type, amount, and properties of the conductive fillers comprising the composition.

In certain embodiments, a sulfur-containing polymer and/or sulfur-containing polymer adduct comprises from about 50 wt% to about 90 wt% of a composition, from about 60 wt% to about 90 wt%, from about 70 wt% to about 90 wt%, and in certain embodiments, from about 80 wt% to about 90 wt% of the composition, where wt% is based on the total dry solids weight of the composition.

A composition may also include any number of additives as desired. Examples of suitable additives include plasticizers, pigments, surfactants, adhesive promoters, thixotropic agents, fire retardants, masking agents, and accelerators (such as amines, including 1,4-diazabicyclo[2.2.2]octane, DABCO®), and combinations of any of the foregoing. When used, the additives may be present in a composition in an amount ranging, for example, from about 0% to 60% by weight. In certain embodiments, additives may be present in a composition in an amount ranging from about 25% to 60% by weight.

Uses

Compositions provided by the present disclosure may be used, for example, in sealants, coatings, encapsulants, and potting compositions. A sealant includes a composition capable of producing a film that has the ability to resist operational conditions, such as moisture and temperature, and at least partially block the transmission of materials, such as water, fuel, and other liquid and gases. A coating composition includes a covering that is applied to the surface of a substrate to, for example, improve the properties of the substrate such as the appearance, adhesion, wettability, corrosion resistance, wear resistance, fuel resistance, and/or abrasion resistance. A potting composition includes a material useful in an electronic assembly to provide resistance to shock and vibration and to exclude moisture and corrosive agents. In certain embodiments, sealant compositions provided by the present disclosure are useful, e.g., as aerospace sealants and as linings for fuel tanks.

In certain embodiments, compositions, such as sealants, may be provided as multi-pack compositions, such as two-pack compositions, wherein one package comprises one or more thiol-terminated polythioethers provided by the present disclosure and a second package comprises one or more poly-functional sulfur-containing epoxies provided by the present disclosure. Additives and/or other materials may be added to either package as desired or necessary. The two packages may be combined and mixed prior to use. In certain embodiments, the pot life of the one or more mixed thiol-terminated polythioethers and epoxies is at least 30 minutes, at least 1 hour, at least 2 hours, and in certain embodiments, more than 2 hours, where pot life refers to the period of time the mixed composition remains suitable for use as a sealant after mixing.

Compositions, including sealants, provided by the present disclosure may be applied to any of a variety of substrates. Examples of substrates to which a composition may be applied include metals such as titanium, stainless steel, and aluminum, any of which may be anodized, primed, organic-coated or chrome-coated; epoxy; urethane; graphite; fiber-glass composite; Kevlar®; acrylics; and polycarbonates. In certain embodiments, compositions provided by the present disclosure may be applied to a coating on a substrate, such as a polyurethane coating.

Compositions provided by the present disclosure may be applied directly onto the surface of a substrate or over an underlayer by any suitable coating process known to those of ordinary skill in the art.

Furthermore, methods are provided for sealing an aperture utilizing a composition provided by the present disclosure. These methods comprise, for example, applying a composition provided by the present disclosure to a surface to seal an aperture, and curing the composition. In certain embodiments, a method for sealing an aperture comprises (a) applying a sealant composition provided by the present disclosure to one or more surfaces defining an aperture, (b) assembling the surfaces defining the aperture, and (c) curing the sealant, to provide a sealed aperture.
In certain embodiments, a composition may be cured under ambient conditions, where ambient conditions refers to a temperature from 20°C to 25°C, and atmospheric humidity. In certain embodiments, a composition may be cured under conditions encompassing a temperature from 0°C to 100°C and humidity from 0% relative humidity to 100% relative humidity. In certain embodiments, a composition may be cured at a higher temperature such as at least 30°C, at least 40°C, and in certain embodiments, at least 50°C. In certain embodiments, a composition may be cured at room temperature, e.g., 25°C. In certain embodiments, a composition may be cured upon exposure to actinic radiation, such as ultraviolet radiation. As will also be appreciated, the methods may be used to seal apertures on aerospace vehicles including aircraft and aerospace vehicles.

In certain embodiments, the composition achieves a tack-free cure in less than about 2 hours, less than about 4 hours, less than about 6 hours, less than about 8 hours, and in certain embodiments, less than about 10 hours, at a temperature of less than about 200°F.

The time to form a viable seal using curable compositions of the present disclosure can depend on several factors as can be appreciated by those skilled in the art, and as defined by the requirements of applicable standards and specifications. In general, curable compositions of the present disclosure develop adhesion strength within 24 hours to 50 hours, and 90% of full adhesion develops from 2 days to 3 days, following mixing and application to a surface. In general, full adhesion strength as well as other properties of cured compositions of the present disclosure becomes fully developed within 7 days following mixing and application of a curable composition to a surface.

Cured compositions disclosed herein, such as cured sealants, exhibit properties acceptable for use in aerospace applications. In general, it is desirable that sealants used in aviation and aerospace applications exhibit the following properties: peel strength greater than 20 pounds per linear inch (psi) on Aerospace Material Specification (AMS) 3265B substrates determined under dry conditions, following immersion in JRF for 7 days, and following immersion in a solution of 3% NaCl according to AMS 3265B test specifications; tensile strength between 300 pounds per square inch (psi) and 400 psi; tear strength greater than 50 pounds per linear inch (psi); elongation between 250% and 300%; and hardness greater than 40 Durometer A. These and other cured sealant properties appropriate for aviation and aerospace applications are disclosed in AMS 3265B, the entirety of which is incorporated herein by reference. It is also desirable that, when cured, compositions of the present disclosure used in aviation and aircraft applications exhibit a percent volume swell not greater than 25% following immersion for one week at 60°C (140°F) and ambient pressure in JRF type 1. Other properties, ranges, and/or thresholds may be appropriate for other sealant applications.

In certain embodiments, therefore, compositions provided by the present disclosure are fuel-resistant. As used herein, the term “fuel resistant” means that a composition, when applied to a substrate and cured, can provide a cured product, such as a sealant, that exhibits a percent volume swell of not greater than 40%, in some cases not greater than 25%, in some cases not greater than 20%, in yet other cases not more than 10%, after immersion for one week at 140°F (60°C) and ambient pressure in Jet Reference Fluid (JRF) Type 1 according to methods similar to those described in ASTM D792 (American Society for Testing and Materials) or AMS 3269 (Aerospace Material Specification), Jet Reference Fluid JRF Type I, as employed for determination of fuel resistance, has the following composition: toluene: 28±1% by volume; cyclohexane (technical): 34±1% by volume; isooctane: 38±1% by volume; and tertiary dibutyl disulfide: 1±0.005% by volume (see AMS 2629, issued Jul. 1, 1989, §3.1.1 et al., available from SAE (Society of Automotive Engineers)).

In certain embodiments, compositions provided herein provide a cured product, such as a sealant, exhibiting a tensile elongation of at least 100% and a tensile strength of at least 400 psi when measured in accordance with the procedure described in AMS 3279, §3.3.17.1, test procedure AS5127/1, §7.7.

In certain embodiments, compositions provide a cured product, such as a sealant, that exhibits a lap shear strength of greater than 200 psi, such as at least 220 psi, at least 250 psi, and, in some cases, at least 400 psi, when measured according to the procedure described in SAE: AS5127/1 paragraph 7.8.

In certain embodiments, a cured sealant comprising a composition provided by the present disclosure meets or exceeds the requirements for aerospace sealants as set forth in AMS 3277.

Apertures, including apertures of aerospace vehicles, sealed with compositions provided by the present disclosure are also disclosed.

In certain embodiments, an electrically conductive sealant composition provided by the present disclosure exhibits the following properties measured at room temperature following exposure at 500°F for 24 hours: a surface resistivity of less than 1 ohms/square, a tensile strength greater than 200 psi, an elongation greater than 100%, and a cohesive failure of 100% measured according to MIL-C-27725.

In certain embodiments, a cured sealant provided by the present disclosure exhibits the following properties when cured for 2 days at room temperature, 1 day at 140°F, and 1 day at 200°F: a dry hardness of 49, a tensile strength of 428 psi, and an elongation of 266%; and after 7 days in JRF, a hardness of 36, a tensile strength of 312 psi, and an elongation of 247%.

In certain embodiments, compositions provided by the present disclosure exhibit a Shore A hardness (7-day cure) greater than 10, greater than 20, greater than 30, and in certain embodiments, greater than 40; a tensile strength greater than 10 psi, greater than 100 psi, greater than 200 psi, and in certain embodiments, greater than 500 psi; an elongation greater than 100%, greater than 200%, greater than 500%, and in certain embodiments, greater than 1,000%; and a swell following exposure to JRF (7 days) less than 20%.

EXAMPLES

Embodiments provided by the present disclosure are further illustrated by reference to the following examples, which describe the synthesis, properties, and uses of certain sulfur-containing polymers, Michael acceptor adducts, and compositions comprising sulfur-containing polymers, Michael acceptor adducts, and Michael acceptors. It will be apparent to those skilled in the art that many modifications, both to materials, and methods, may be practiced without departing from the scope of the disclosure.

Example 1
Polyether Cured with Monomeric Divinyl Sulfone

To prepare Resin Mixture A, thiol-terminated polythioethers of the type described in U.S. Pat. No. 6,172,179, average thiol functionality: 2.05-2.95, commercially available from
PRC-Desoto International, Inc., Sylmar, Calif., HB-40 plasticizer (Solutia Inc.), DABCO® 33L (Huntsman), Winmore® SPM (Solvay), Sipermut® D13 (Evonik) and tung oil (Alnor Oil Company, Inc.) were added to a Max 300 (FlackTek) jar in the order and amounts listed in Table 1. The materials were mixed with a DAC 600.1 FVZ mixer (Flack-Tek) for 45 seconds. Vinyl sulfone (Aldrich) (4.99 g) was then added to Resin Mixture A and mixed for 1 minute. The mixture was immediately poured onto polyethylene sheets and pressed out flat to form a ¼" sheets. Samples were cured for two weeks at room temperature. The sheet material was then tested for hardness, tensile strength, elongation, and fluid resistance. The results are provided in Table 2.

**TABLE 1**

<table>
<thead>
<tr>
<th>Material</th>
<th>Amount (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polythioether*</td>
<td>140.05</td>
</tr>
<tr>
<td>HB-40</td>
<td>1.18</td>
</tr>
<tr>
<td>DABCO® 33L</td>
<td>1.58</td>
</tr>
<tr>
<td>Winmore® SPM</td>
<td>43.08</td>
</tr>
<tr>
<td>Sipermut® D13</td>
<td>9.11</td>
</tr>
</tbody>
</table>

*Polythioether of the type described in U.S. Pat. No. 5,727,178; average thiol functionality 2.05-2.25, commercially available from PRC-Desoto International, Inc., Sylmar, CA.

**TABLE 2**

<table>
<thead>
<tr>
<th>Test</th>
<th>Description</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dureometer</td>
<td>ASTM D 2240</td>
<td>53</td>
</tr>
<tr>
<td>Elongation</td>
<td>ASTM D 412</td>
<td>390%</td>
</tr>
<tr>
<td>Tensile Strength</td>
<td>ASTM D 412</td>
<td>3006 Kpas</td>
</tr>
<tr>
<td>Swell, distilled</td>
<td>SAE AS5271/1 7.4</td>
<td>8.5%</td>
</tr>
<tr>
<td>Swell, NaCl</td>
<td>SAE AS5271/1 7.4</td>
<td>3%</td>
</tr>
<tr>
<td>Swell, JRF</td>
<td>SAE AS5271/1 7.4</td>
<td>16.7%</td>
</tr>
</tbody>
</table>

Example 2

**Polysulfide Polymer Cured with Monomeric Divinyl Sulfone**

Mixing was performed in a 60-g plastic container with a lid. Divinyl sulfone (1.22 g), triethylenediamine (0.17 g) and Thiokol LP-32 (33.01 g, a liquid polysulfide polymer available from Toray Fine Chemicals) were added to the 60-g container. The container was placed in a mixer (DAC 600 FVZ) and mixed for 60 seconds at 2,300 rpm. The mixed material was cured inside the plastic container for 7 days at room temperature. After 7 days, the hardness of the cured material was 14 Shore A, measured according to ASTM D 2240.

Example 3

**Polythioether Cured with Monomeric Divinyl Sulfone**

Divinyl sulfone (3.05 g), triethylenediamine (0.39 g) and Permapol® P3.1E (74.18 g, a thiol-terminated polythioether polymer available from PRC-Desoto International, Inc., Sylmar, Calif.) were added to a plastic container. The container was placed in a mixer (DAC 600 FVZ) and mixed for 60 seconds at 2,300 rpm. A portion of the mixed material was cured inside the plastic container for 7 days at room temperature. After 7 days, the hardness of the cured material was 42 Shore A, measured according to ASTM D 2240.

A second portion of the mixed material was poured onto a 12"x18"x¼" flat glass substrate and pressed to form a uniform ¼"-thick sheet. The sheet was cured for 7 days at ambient conditions. The cured sheet had a tensile strength of 696 psi and an elongation of 933%. The tensile strength and elongation were measured according to ASTM D 412.

Example 4

**Polythioether Cured with Divinyl Sulfone**

Divinyl sulfone (3.05 g), triethylenediamine (0.62 g), Permapol® P3.1E (74.70 g, a thiol-terminated polythioether polymer available from PRC-Desoto International, Inc., Sylmar, Calif.), and calcium carbonate (48.50 g) were added to a 100-gram plastic container. The container was placed in a mixer (DAC 600 FVZ) and mixed for 60 seconds at 2,300 rpm. A portion of the mixed material was cured inside the plastic container for 7 days at room temperature. After 7 days, the hardness of the cured material was 25 Shore A, measured according to ASTM D 2240.

A second portion of the mixed material was poured onto a 12"x18"x¼" flat glass substrate and pressed to form a uniform ¼"-thick sheet. The sheet was cured for 7 days at ambient conditions. The cured sheet had a tensile strength of 546 psi and an elongation of 1,077%. The tensile strength and elongation were measured according to ASTM D 412.

Example 5

**Synthesis of Divinyl Sulfone-Terminated Polythioether Adduct**

In a 300 mL, 3-necked, round bottom flask fitted with a mechanical stirrer, thiol-terminated polythioether polymer Permapol® P3.1E (149.40 g, available from PRC-Desoto International, Inc., Sylmar, Calif.), divinyl sulfone (12.18 g), and triethylenediamine (0.81 g) were added at room temperature. The mixture was stirred for 10 minutes, resulting in a vinyl sulfone-terminated polythioether adduct that had a viscosity of 309.0 poise. The viscosity was measured by CAP2000 viscometer with spindle #6, 50 RPM.

Example 6

**Polythioether Michael Acceptor Adduct Cured with a Thiol-Terminated Polysulfide Polymer**

Mixing was performed in a 60-gram plastic container with lid. The adduct from Example 5 (9.27 g) and Thiokol LP-980 (5.90 g, a liquid polysulfide polymer, available from Toray Fine Chemicals) were added to the 60-gram container. The container was in a mixer (DAC 600 FVZ) and mixed for 60 seconds at 2,300 rpm. The mixed material was cured inside the plastic container for 7 days at room temperature. After 7 days, hardness of the cured material was 11 Shore A and volume swell percentage in jet reference fluid type 1 (JRF Type 1) of cured material was 19.20%. Hardness and volume...
swell percentage in jet reference fluid type I (JRF Type I) were measured according to ASTM D 2240 and SAE AS5127/1 Section 7.4, respectively.

Example 7

Polythioether Michael Acceptor Adduct Cured with a Thiol-Terminated Polysulfide Polymer

Mixing was performed in a 60-g plastic container with lid. The adduct from Example 5 (9.27 g) and Thiokol LP-32 (9.17 g, a liquid polysulfide polymer, available from Toray Fine Chemicals) were added to the 60-g container. The container was placed in a mixer (DAC 600 VFZ) and mixed for 60 seconds at 2,300 rpm. The mixed material was cured inside the plastic container for 7 days at room temperature. After 7 days, hardness of cured material is 24 Shore A and volume swell percentage in jet reference fluid type I (JRF Type I) of cured material is 18.81%. Hardness and volume swell percentage in jet reference fluid type I (JRF Type I) were measured according to ASTM D 2240 and SAE AS5127/1 Section 7.4, respectively.

Example 8

Polythioether Michael Acceptor Adduct Cured with a Thiol-Terminated Polysulfide Polymer

Mixing was performed in a 60-gm plastic container with lid. The adduct from Example 5 (9.27 g) and Thiokol LP-12 (9.17 g, a liquid polysulfide polymer, available from Toray Fine Chemicals) were added to the 60-gm container. The container was placed in a mixer (DAC 600 VFZ) and mixed for 60 seconds at 2,300 rpm. The mixed material was cured inside the plastic container for 7 days at room temperature. After 7 days, hardness of cured material is 25 Shore A and volume swell percentage in jet reference fluid type I (JRF Type I) of cured material is 19.41%. Hardness and volume swell percentage in jet reference fluid type I (JRF Type I) were measured according to ASTM D 2240 and SAE AS5127/1 Section 7.4, respectively.

Example 9

Polythioether Michael Acceptor Adduct Cured with a Thiol-Terminated Polysulfide Polymer

Mixing was performed in a plastic container with lid. The adduct from Example 5 (74.13 g) and Thioplast® G21 (48.80 g, a liquid polysulfide polymer, available from Akzo Nobel) were added to the container. The container was placed in a mixer (DAC 600 VFZ) and mixed for 60 seconds at 2,300 rpm. A portion of the mixed material was cured inside the plastic container for 7 days at room temperature. After 7 days, hardness of cured material is 32 Shore A and volume swell percentage in jet reference fluid type I (JRF Type I) of cured material is 18.48%. Hardness and volume swell percentage in jet reference fluid type I (JRF Type I) were measured according to ASTM D 2240 and SAE AS5127/1 Section 7.4, respectively.

A second portion of the mixed material was poured onto a 12"x18"x½" flat glass substrate and pressed to form a uniform ½"-thick sheet. The sheet was cured for 7 days at ambient conditions. The cured sheet had a tensile strength of 88 psi and an elongation of 107%. The tensile strength and elongation were measured according to ASTM D412.

Example 10

Polythioether Michael Acceptor Adduct Cured with a Thiol-Terminated Polysulfide Polymer

The mixing was performed in a plastic container with lid. The adduct from Example 5 (74.13 g) and Thioplast® G21 (48.80 g, a liquid polysulfide polymer, available from Akzo Nobel) were added to the container. The container was placed in a mixer (DAC 600 VFZ) and mixed for 60 seconds at 2,300 rpm. A portion of the mixed material was cured inside the plastic container for 7 days at room temperature. After 7 days, hardness of cured material is 32 Shore A and volume swell percentage in jet reference fluid type I (JRF Type I) of cured material is 18.48%. Hardness and volume swell percentage in jet reference fluid type I (JRF Type I) were measured according to ASTM D 2240 and SAE AS5127/1 Section 7.4, respectively.

A second portion of the mixed material was poured onto a 12"x18"x½" flat glass substrate and pressed to form a uniform ½"-thick sheet. The sheet was cured for 7 days at ambient conditions. The cured sheet had a tensile strength of 88 psi and an elongation of 107%. The tensile strength and elongation were measured according to ASTM D412.

Example 11

Polythioether Michael Acceptor Adduct Cured with a Thiol-Terminated Polysulfide Polymer

The mixing was performed in a plastic container with lid. The adduct from Example 5 (74.13 g) and Thioplast® G21 (48.80 g, a liquid polysulfide polymer, available from Akzo Nobel) were added to the container. The container was placed in a mixer (DAC 600 VFZ) and mixed for 60 seconds at 2,300 rpm. A portion of the mixed material was cured inside the plastic container for 7 days at room temperature. After 7 days, hardness of cured material is 32 Shore A and volume swell percentage in jet reference fluid type I (JRF Type I) of cured material is 18.48%. Hardness and volume swell percentage in jet reference fluid type I (JRF Type I) were measured according to ASTM D 2240 and SAE AS5127/1 Section 7.4, respectively.

A second portion of the mixed material was poured onto a 12"x18"x½" flat glass substrate and pressed to form a uniform ½"-thick sheet. The sheet was cured for 7 days at ambient conditions. The cured sheet had a tensile strength of 88 psi and an elongation of 107%. The tensile strength and elongation were measured according to ASTM D412.

Example 12

Polythioether Michael Acceptor Adduct Cured with a Thiol-Terminated Polysulfide Polymer

The mixing was performed in a plastic container with lid. The adduct from Example 5 (74.13 g) and Permapol® P3,1E (29.96 g, a thiol-terminated polythioether polymer available from PRC-Desoto International Inc., Sylmar, Calif.), and tri-ethylene diamine (0.31 g) were added to the container. The container was placed in a mixer (DAC 600 VFZ) and mixed for 60 seconds at 2,300 rpm. A portion of the mixed material was cured inside the plastic container for 7 days at room temperature. After 7 days, hardness of cured material is 31 Shore A. Hardness was measured according to ASTM D 2240.
A second portion of the mixed material was poured onto a 12\"x18\"x\(\frac{1}{4}\)" flat glass substrate and pressed to form a uniform \(\frac{1}{4}\)"-thick sheet. The sheet was cured for 7 days at ambient conditions. The cured sheet had a tensile strength of 446 psi and an elongation of 504%. The tensile strength and elongation were measured according to ASTM D412.

Example 13

Polythioether Michael Acceptor Adduct Cured with a Thiol-Terminated Polythioether Polymer

A sealant was produced according to the composition shown in Table 1.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Charge weight, g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Example 5 adduct</td>
<td>34.17</td>
</tr>
<tr>
<td>Permapol® P3.1E</td>
<td>29.96</td>
</tr>
<tr>
<td>Carbon Black</td>
<td>20.00</td>
</tr>
<tr>
<td>Triethylendiamine</td>
<td>0.32</td>
</tr>
</tbody>
</table>

The mixing was performed in a 100-gram plastic container with lid. The adduct from Example 5 (34.17 g), Permapol® P3.1E (29.96 g), a thiol-terminated polythioether polymer, available from PRC-Desoto International Inc., Sylmar, Calif., carbon black (20.00 g), and triethylendiamine (0.32 g) were added to the 100-gram container. The container was placed in a mixer (DAC 600 FVZ) and mixed for 60 seconds at 2,300 rpm. A portion of the mixed material was cured inside the plastic container for 7 days at room temperature. After 7-day cure, hardness of cured material is 43 Shore A, measured according to ASTM D 2240.

A second portion of the mixed material was poured onto a 12\"x18\"x\(\frac{1}{4}\)" flat glass substrate and pressed to form a uniform \(\frac{1}{4}\)"-thick sheet. The sheet was cured for 7 days at ambient conditions. The cured sheet had a tensile strength of 1810 psi and an elongation of 950%. The tensile strength and elongation were measured according to ASTM D412.

Example 14

Polythioether Michael Acceptor Adduct Cured with a Thiol-Terminated Polythioether Polymer, Low Density

A sealant was produced according to the composition shown in Table 2.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Charge weight, g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Example 5 adduct</td>
<td>34.17</td>
</tr>
<tr>
<td>Permapol® P3.1E</td>
<td>29.96</td>
</tr>
<tr>
<td>Carbon Black</td>
<td>7.20</td>
</tr>
<tr>
<td>Triethylendiamine</td>
<td>0.32</td>
</tr>
<tr>
<td>Duolite® E135-040D</td>
<td>7.20</td>
</tr>
</tbody>
</table>

The mixing was performed in a 100-gram plastic container with lid. The adduct from Example 5 (34.17 g), Permapol® P3.1E (29.96 g), a thiol-terminated polythioether polymer, available from PRC-Desoto International Inc., Sylmar, Calif., carbon black (7.20 g), triethylendiamine (0.32 g) and Duolite® E135-040D (7.20 g), available from Henkel), were added to the 100-gram container. The container was placed in a mixer (DAC 600 FVZ) and mixed for 60 seconds at 2,300 rpm. A portion of the mixed material was cured inside the plastic container for 7 days at room temperature. After 7 days, hardness of cured material is 35 Shore A, measured according to ASTM D 2240.

A second portion of the mixed material was poured onto a 12\"x18\"x\(\frac{1}{4}\)" flat glass substrate and pressed to form a uniform \(\frac{1}{4}\)"-thick sheet. The sheet was cured for 7 days at ambient conditions. The cured sheet had a tensile strength of 252 psi and an elongation of 772%. The tensile strength and elongation were measured according to ASTM D412. The estimated specific gravity was 0.706.

Example 15

Polythioether Michael Acceptor Adduct Cured with a Thiol-Terminated Polythioether and Epoxy Blend

The mixing was performed in a 60-gm plastic container with lid. The adduct from Example 5 (16.28 g) and Permapol® P3.1E (29.96 g), a thiol-terminated polythioether polymer, available from PRC-Desoto International Inc., Sylmar, Calif.), triethylendiamine (0.23 g), and Novolac® DENTM 431 (1.75 g, an epoxy resin available from Dow Chemical, Midland, Mich.) were added to the 60-gram container. The container was placed in a speed mixer (DAC 600 FVZ) and mixed for 60 seconds for 2,300 rpm. A portion of the mixed material was cured inside the plastic container for 7 days at room temperature. After 7-day cure, hardness of cured material is 35 Shore A, measured according to ASTM D 2240.

A second portion of the mixed material was poured onto a 12\"x18\"x\(\frac{1}{4}\)" flat glass substrate and pressed to form a uniform \(\frac{1}{4}\)"-thick sheet. The sheet was cured for 7 days at ambient conditions. The cured sheet had a tensile strength of 228 psi and an elongation of 176%. The tensile strength and elongation were measured according to ASTM D412.

Example 16

Polythioether Michael Acceptor Adduct Cured with a Thiol-Terminated Polythioether and Isocyanate Blend

The mixing was performed in a 60-gram plastic container with lid. The adduct from Example 5 (33.04 g), Permapol® P3.1E (38.05 g), a thiol-terminated polythioether polymer, available from PRC-Desoto International Inc., Sylmar, Calif.), and an isocyanate-terminated prepolymer (5.0 g, Example 5 of U.S. application Ser. No. 13/050,988). The container was placed in a speed mixer (DAC 600 FVZ) and mixed for 60 seconds for 2,300 rpm. A portion of the mixed material was allowed to cure inside the plastic container for 7 days at room temperature. After 7-day cure, hardness of cured material is 35 Shore A, measured according to ASTM D 2240.

A second portion of the mixed material was poured onto a 12\"x18\"x\(\frac{1}{4}\)" flat glass substrate and pressed to form a uniform \(\frac{1}{4}\)"-thick sheet. The sheet was cured for 7 days at ambient conditions. The cured sheet has a tensile strength of 309 psi and elongation of 576%. The tensile strength and elongation were measured per ASTM D412.
A second portion of the mixed material was poured onto a 12"x12"x1/4" flat glass substrate and pressed to form a uniform ½"-thick sheet. The sheet was cured for 7 days at ambient conditions. The cured sheet had a tensile strength of 562 psi and an elongation of 1170%. The tensile strength and elongation were measured according to ASTM D412.

Example 19
Polythioether Michael Acceptor Adduct Cured with a Diamine

The divinyl sulfone-terminated polythioether adduct from Example 5 (83.99 g), isophorone diamine (4.26 g) and Cab-O-Sil M5 (3.68 g) were added to a plastic container. The container was placed in a mixer (DAC 600 FVZ) and the contents mixed for 60 seconds at 2,300 rpm. A portion of the mixed material was cured inside the plastic container for 7 days at room temperature. After 7 days, the hardness of cured material measured according to ASTM D 2240 was 20 Shore A.

A second portion of the mixed material was poured onto a 12"x12"x1/4" flat glass substrate and pressed to form a uniform ½"-thick sheet. The sheet was cured for 7 days at ambient conditions. The cured sheet had a tensile strength of 420 psi and an elongation of 1209%. The tensile strength and elongation were measured according to ASTM D412.

Example 20
Polythioether Michael Acceptor Adduct Cured with a Blocked Diamine

The adduct from Example 5 (16.80 g), Vestamin® A 139 (1.39 g, available from Evonik) and triethylendiamine (0.27 g) were added to a plastic container. The container was placed in a mixer (DAC 600 FVZ) and mixed for 60 seconds at 2,300 rpm. A portion of the mixed material was cured in the plastic container for 5 weeks at ambient conditions. After 5 weeks, the mixed material cured, forming a solid elastomer.

Finally, it should be noted that there are alternative ways of implementing the embodiments disclosed herein. Accordingly, the present embodiments are to be considered as illustrative and not restrictive. Furthermore, the claims are not to be limited to the details given herein, and are entitled their full scope and equivalents thereof.

What is claimed is:

1. A polythioether adduct comprising at least two terminal Michael acceptor groups, wherein:
the polythioether adduct comprises a polythioether adduct of Formula (3), a polythioether adduct of Formula (3a), or a combination thereof:

\[
\begin{align*}
\text{R}^2 & - \text{S} - \text{R}^1 & \to & \text{S} - (\text{CH}_2)_p - \text{O} - (\text{R}^2 - \text{O})_q - (\text{CH}_2)_r \\
\text{S} & - \text{R}^1 & \to & \text{S} - \text{R}^2 \\
\text{R}^2 & - \text{S} - \text{R}^1 & \to & \text{S} - (\text{CH}_2)_p - \text{O} - (\text{R}^2 - \text{O})_q - (\text{CH}_2)_r \tag{3}
\end{align*}
\]

\[
\begin{align*}
\text{R}^2 & - \text{S} - \text{R}^1 & \to & \text{S} - (\text{CH}_2)_p - \text{O} - (\text{R}^2 - \text{O})_q - (\text{CH}_2)_r \\
\text{S} & - \text{R}^1 & \to & \text{S} - \text{R}^2 \\
\text{R}^2 & - \text{S} & \to & \text{S} - (\text{CH}_2)_p - \text{O} - (\text{R}^2 - \text{O})_q - (\text{CH}_2)_r \tag{3a}
\end{align*}
\]

wherein:
each R^1 independently is selected from C_{2-10} alkanediyl, C_{6-8} cycloalkanediyl, C_{6-12} alkenecycloalkanediyl, C_{5-9} heterocycloalkanediyl, and \{-(\text{CHR}^1)^a - \text{CHR}^2 - \text{CHR}^3 - \}^b, wherein:
s is an integer from 2 to 6;
q is an integer from 1 to 5;
r is an integer from 2 to 10;
each R^2 is independently selected from hydrogen and methyl; and

each X is independently selected from —O—, —S—, and —NR—, wherein R is selected from hydrogen and methyl; each R² is independently selected from C₁₋₁₀ alkanediyl, C₆₋₈ cycloalkanediyl, C₁₀₋₁₄ alkanecycloalkanediyl, and -(CHR⁻¹)-X—][-(CHR⁻²)-], wherein s, q, r, R², and X are as defined for R¹; m is an integer from 0 to 50; n is an integer from 1 to 60; p is an integer from 2 to 6; B represents a core of a z-valent, vinyl-terminated polyfunctionalizing agent B(—V), wherein: z is an integer from 3 to 6; and each —V is a group comprising a terminal vinyl group; and each —V— is derived from the reaction of —V with a thiol.

2. The polythioether adduct of claim 1, wherein the polythioether adduct comprises the reaction products of reactants comprising:
(a) a thiol-terminated polythioether polymer; and
(b) a compound comprising a Michael acceptor group and a group that is reactive with the thiol-terminated polythioether polymer, wherein the Michael acceptor group comprises a vinyl ketone, a vinyl sulfone, a quinone, an enamine, a ketimine, an aldimine, or an oxazolidine.

3. The polythioether adduct of claim 2, wherein the thiol-terminated polythioether polymer comprises a thiol-terminated polythioether polymer of Formula (4), a thiol-terminated polythioether polymer of Formula (4α), or a combination thereof:

\[
\text{R}^{-4} \text{S}^{-1} \text{S}^{-1} \text{R}^{-2} \text{O}_{2n}^{-} \text{(CH₃)₂}^{-} \text{O}^{-}\text{(R}^{-2} \text{O}_{2n}^{-} \text{(CH₃)₂}^{-} \text{S}}^{-3} \text{S}^{-1} \text{S}^{-1} \text{S}^{-1} \text{SH}
\]

(4)

wherein:

- each R² is independently selected from C₂₋₁₀ alkanediyl, C₆₋₈ cycloalkanediyl, C₁₀₋₁₄ alkanecycloalkanediyl, C₁₀₋₁₄ heterocycloalkanediyl, and -(CHR⁻¹)-X—][-(CHR⁻²)-], wherein s, q, r, R², and X are as defined for R¹; m is an integer from 0 to 50; n is an integer from 1 to 60; p is an integer from 2 to 6; B represents a core of a z-valent, vinyl-terminated polyfunctionalizing agent B(—V), wherein: z is an integer from 3 to 6; and each —V is a group comprising a terminal vinyl group; and each —V— is derived from the reaction of —V with a thiol.

4. A composition comprising:
(a) the polythioether adduct of claim 1; and
(b) a compound having at least two Michael acceptor groups, wherein the compound having at least two Michael acceptor groups has a molecular weight less than 400 Daltons.

5. The composition of claim 4 comprising a polyepoxy.

6. The composition of claim 4 comprising a polyisocyanate comprising isocyanate groups, wherein the isocyanate groups are less reactive with Michael acceptor groups than with thiol groups.

7. The composition of claim 4 comprising a polysulfide polymer comprising at least two terminal groups reactive with Michael acceptor groups.

8. A composition comprising:
(a) the polythioether adduct of claim 1; and
(b) a curing agent comprising at least two terminal groups that are reactive with Michael acceptor groups.

9. The composition of claim 8, wherein the curing agent comprises a sulfur-containing polymer comprising at least two terminal groups reactive with Michael acceptor groups, a monomeric thiol, a polythiol, a polyamine, a blocked amine, or a combination of any of the foregoing.

10. The composition of claim 8, wherein the curing agent comprises a sulfur-containing polymer comprising at least two terminal groups reactive with Michael acceptor groups.

11. The composition of claim 10, wherein the sulfur-containing polymer comprises a polythioether.

12. The composition of claim 11, wherein the polythioether comprises a thiol-terminated polythioether polymer of Formula (4), a thiol-terminated polythioether polymer of Formula (4α), or a combination thereof:

\[
\text{R}^{-4} \text{S}^{-1} \text{S}^{-1} \text{R}^{-2} \text{O}_{2n}^{-} \text{(CH₃)₂}^{-} \text{O}^{-}\text{(R}^{-2} \text{O}_{2n}^{-} \text{(CH₃)₂}^{-} \text{S}}^{-3} \text{S}^{-1} \text{S}^{-1} \text{S}^{-1} \text{SH}
\]

(4α)

wherein:

- each R² is independently selected from C₂₋₁₀ alkanediyl, C₆₋₈ cycloalkanediyl, C₁₀₋₁₄ alkanecycloalkanediyl, C₁₀₋₁₄ heterocycloalkanediyl, and -(CHR⁻¹)-X—][-(CHR⁻²)-], wherein s, q, r, R², and X are as defined for R¹; m is an integer from 0 to 50; n is an integer from 1 to 60; p is an integer from 2 to 6; B represents a core of a z-valent, vinyl-terminated polyfunctionalizing agent B(—V), wherein: z is an integer from 3 to 6; and each —V is a group comprising a terminal vinyl group; and each —V— is derived from the reaction of —V with a thiol.

13. The composition of claim 10, wherein the sulfur-containing polymer comprises a polysulfide polymer.
14. The composition of claim 8, comprising a polyepoxy.
15. The composition of claim 8, comprising a polyisocyanate comprising isocyanate groups, wherein the isocyanate groups are less reactive with Michael acceptor groups than with thiol groups.
16. The composition of claim 8, comprising a polysulfide adduct.
17. A composition comprising:
   (a) a sulfur-containing adduct containing at least two Michael acceptor groups, wherein the sulfur-containing adduct comprises the polythioether adduct of claim 1;
   (b) a sulfur-containing polymer comprising at least two terminal groups reactive with Michael acceptor groups; and
   (c) a monomeric compound having at least two Michael acceptor groups.
18. A hydroxyl-terminated sulfur-containing adduct comprising the reaction products of reactants comprising:
   (a) a sulfur-containing Michael acceptor adduct comprising at least two terminal Michael acceptor groups, wherein the sulfur-containing Michael acceptor adduct comprises the polythioether adduct of claim 1; and
   (b) a compound having a hydroxyl group and a group that is reactive with the terminal groups of the sulfur-containing Michael acceptor adduct.
19. A composition comprising:
   (a) the hydroxyl-terminated sulfur-containing adduct of claim 18; and
   (b) a polyisocyanate curing agent.
20. An amine-terminated sulfur-containing adduct comprising the reaction products of reactants comprising:
   (a) a sulfur-containing Michael acceptor adduct comprising at least two terminal Michael acceptor groups, wherein the sulfur-containing Michael acceptor adduct comprises the polythioether adduct of claim 1; and
   (b) a compound having an amine group and a group that is reactive with the terminal groups of the sulfur-containing Michael acceptor adduct.
21. A composition comprising:
   (a) the amine-terminated sulfur-containing adduct of claim 20; and
   (b) a polyisocyanate curing agent.

* * * * *